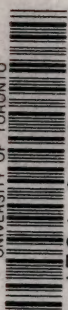



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THE ANALYSIS OF COPPER

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THE
"ANALYSIS OF COPPER"

AND
ITS ORES AND ALLOYS "

BY
GEORGE L. 'HEATH'
CHIEF CHEMIST, CALUMET & HECLA SMELTING WORKS
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FIRST EDITION

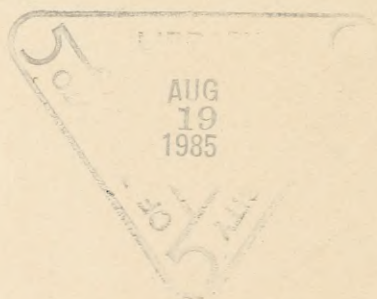
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PREFACE

THIS volume constitutes the first connected representative account of the principal methods employed by the largest refineries, foundries, and custom sampling works for the control of operations and valuation of material, following the logical sequence from the ore in the mine to the finished metallic product. The book is accordingly intended, primarily, for the technical chemist and advanced student.

As there is considerable similarity in methods of assaying adopted at reduction works situated west of the Mississippi river in the United States, the methods reported by the largest concerns will be designated, by request, as "Western methods."

Comparatively recent papers by engineers and chemists have emphasized the fact that the correct sampling is an absolute necessity. In consequence, a special feature has been made of this subject, although it has been neglected in other chemical books. A scheme for the sampling of coal on a large scale has been included, but the analytical work has been omitted because a book on this special subject has recently been published.

The author takes pleasure in giving credit where it is due by recording the names of those who have shown an interest in making the account representative of the latest practice of the large producers and consumers of copper, or have contributed material which has been included in the text. Among these are the late J. B. Cooper and M. B. Patch, formerly Supts. of C. & H. refineries; E. P. Mathewson, Mgr., and Chief Chemist, Anaconda Co.; Dr. E. Keller, Perth Amboy, N. J.; W. H. Bassett, Technical Supt., Alden Merrill, Chemist, American Brass Co.; C. H. Benedict, Metallurgist, C. & H. Mining Co.; J. R. Agnew, Supt. and J. W. Rawlins, Chemist, Canadian Copper Co.; A. Alexander, Mgr., F. Andrews, Chief Chemist, Raritan Copper Works; A. M. Smoot (Ledoux & Co.), New York; L. Addicks, Douglas, Ariz.; F. D. Greenwood, Chief Chemist, U. S. Metals Refining Co.; J. Klein, Chemist, Buffalo Rolling Mill; R. Franke, Director, and H. Koch, Chief Chemical Inspector, Mansfeld Works, Eisleben.

Dr. Toisten, Chemist of the Mansfeld Brass Works, Hettstedt, Germany; Prof. R. H. Richards and Prof. C. R. Hayward, Boston. Valuable aid has also been received from assistants in the modification of two or three methods, and from the papers of F. P. Dewey, W. C. Ferguson, F. G. Hawley, G. C. Stone, and others.

June, 1916

GEORGE L. HEATH

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ANALYSIS OF COPPER

PART I

CHAPTER I

INTRODUCTION

1. Although the principal title of this book is the "Analysis of Copper," the treatment of the subject is more comprehensive and includes the analysis of copper bearing minerals, mattes, slags, and other metallurgical products. In this connection methods are given for the quantitative determination of most of the common metallic elements and for some of the rarer ones. The chapters are divided into five groups, the arrangement of the subject matter following the progress of the copper from the mine to the finished product. The standard methods used in western ore-reduction works are designated by request as "Western methods," and when two or more methods are included for the estimation of a single constituent, the first is to be preferred unless the field of each is specified. All are standard methods in use at some one of the larger plants but the operator without special experience is advised to select the one prescribed for the particular material treated, and neither to omit any steps in a process nor to use a limited method outside of its prescribed field, except after careful experiment.

No attempt is made to give a complete list of apparatus used in metallurgical analysis but a few special improvements which have been adopted in large copper laboratories to facilitate rapid work are described. All apparatus should be suited to the character of the work, whether it be ore-assaying or the delicate estimation of traces of impurities in refined metal, an operation in which results are calculated to a ten-thousandth of one per cent, or one more decimal place than is usual in reporting tests of iron and steel. To permit this degree of accuracy in the examination of refined copper, the bulk of final solutions and the size of filter papers and containers should be kept as small as possible without undue sacrifice of speed.

SPECIAL EQUIPMENT

2. Office Records. — Large works keep a systematic record of all tests except for those of temporary character. A serial number is given to every sample that comes to the laboratory, and printed cards or tickets are provided upon which are entered all the data of weights, sampling, and analysis. These records are subsequently bound, catalogued, and filed away for ready reference. A few plants have adopted a system of 5×8 inch tabbed cards which are filed in cases, each drawer holding 1000 cards. The U. S. Metals Refining Co. use a triplicate series of tickets, on which the descriptions are entered by a clerk to relieve the chemists. The assay slips are printed in three colors, white, red, and yellow, with carbon papers between them. The white slip is filed eventually in the clerk's office, the red slip is sent to the laboratory with the sample, and the yellow one to the assay department. After the chemist in charge has checked the work and signed the assay certificate filled in by the clerk, the yellow and red slips are filed in the laboratory.

The work of the Mansfeld Smelter in Germany is of a peculiar nature. The ore deposits are partly surface slates and partly true ores which contain a refractory mineral "typolite." In addition to daily reports, the completeness of German system requires that the chief chemist shall furnish a monthly thirty-page report of all the work of the month, including the ore and metal returns of mines, electrolytic refinery, and brass works.

3. Assay Furnaces of portable type are a necessity in remote places. The best of coal or gas fired muffle and pot furnaces are the rule in modern plants. A plan of a good pot furnace, adapted to either native copper or gold ores, is inserted. The depth of the furnace from cover to grate is 61 cm. and the grate area 32×46 cm. The ash-pit door is made with an extra weight, so that a blast of air may be admitted under the grate through a pipe 6.3 cm. in diameter. The air may be furnished by the smallest Roots' blower, belted to a shaft in the sampling room and driven by a small five-horse power electric motor.

4. The Furnace Accessories, devised by Dr. E. Keller, are of assistance in rapid work, especially on bullion.¹ A *cupel charger*

¹ *Trans. A. I. M. E.* 36 (1906), 3.

permits 48 cupels to be placed, or withdrawn, as a unit. The front row of assays are blanks, the other 40 being charged with the lead buttons. *Other devices* are parting baths with holders, multiple scorifier tongs, a stirring machine to be used with

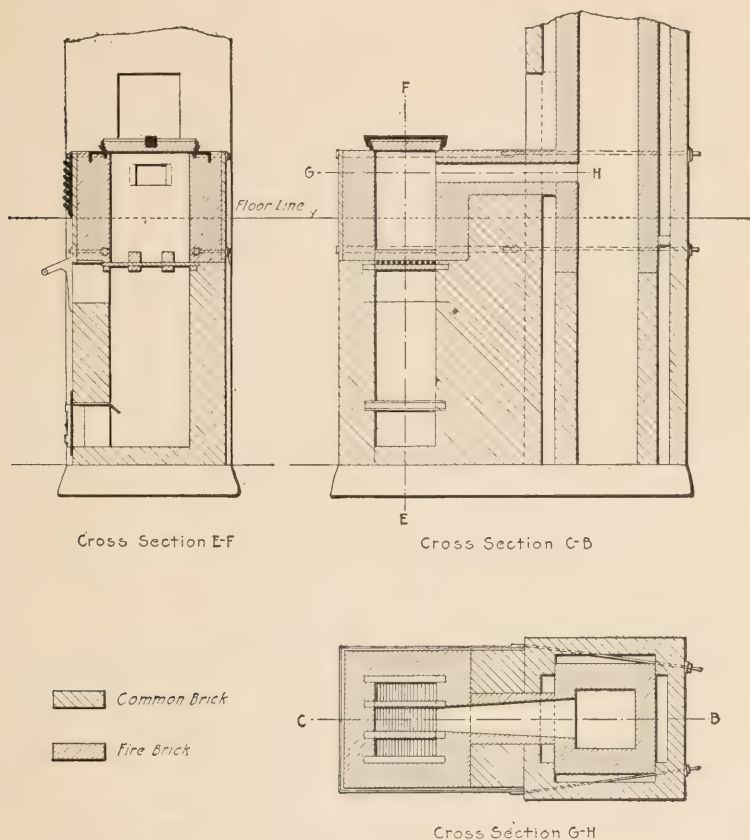


Fig. 1. — Assay Furnace.

beakers, and a mechanical filtration apparatus in which 20 silver assays, contained in 750 c.c. beakers, may be filtered simultaneously. Although *riffls* of correct design are easily purchased, they are quickly and cheaply made. Haultain has described their manufacture.¹

¹ *Eng. and Min. Jour.* 73 (1907), 232.

APPARATUS — STANDARD FLASKS AND ALIQUOTING
PIPETTES

5. Copper Flasks, as they are called, and automatic “wash-out” pipettes are used in the electrolytic assay of crude copper. Water-jacketed “delivery pipettes” have been described by W. C. Ferguson of the Nichols Co.¹ A. M. Smoot gives the following directions for his simple “wash-out” pipette, to which the liter “copper flasks” are adjusted in mutual agreement.



Fig. 2. — Liter
Flask for Copper
Assay.

“In assaying inhomogeneous materials, such as blister or converter borings, which consist of roughly pulverized coarse and fine parts differing from each other in composition, it is necessary to weigh out a charge large enough to cover the variations. In some cases, a preliminary separation of the coarse and fine parts of the whole sample is essential. The charge for assay is then formed by taking proportionate weights of each part. In any case, the sample to be weighed for assay will be larger than can be conveniently electrolyzed directly.

“Aliquoting apparatus is therefore necessary, but the ordinary flask and hand pipette are not sufficiently accurate. Measurements within an error of one or two hundredths of a per cent are essential in dividing strong solutions of material rich in copper. A convenient liter flask is shown in Fig. 2 and the pipette in Fig. 3.

“The flask has an enlarged neck which not only facilitates the introduction of the sample and reagents, but also renders the mixing of the solutions much easier when the volume is made up to the mark. The necks of these flasks below the enlargement should be narrow, so that the meniscus may be clearly defined against the mark.

“Mechanical pipettes² with an automatic zero point may also be made to deliver the required volume, but in order to retain the required accuracy, such pipettes must be rigidly mounted to



Fig. 3. —
Pipette.

¹ *J. Ind. and Eng. Chem.* 2 (1910), 187.

² *Ibid.*

prevent vibration, and must be kept scrupulously clean, since a trace of adhering dirt or grease will make a difference in the volume actually delivered. Such delivery pipettes are usually provided with a lower stop cock, and the slightest variation from the perpendicular in opening it will retard the flow of liquid, causing a slight error. Each form of pipette has its advocates.

"*Hand Pipettes* may be used if carefully compared and constructed to *hold* instead of deliver an aliquot part of the contents of the flasks, and if the pipette is subsequently washed out."

The *Smoot pipette* (Fig. 3) has a stop cock which itself serves as an automatic zero point. When the pipette is full, it holds an exact fraction of the contents of the liter flask from the bottom of the stop cock to the end of delivery tube. On turning the valve through an angle of 45° , air is admitted through the funnel, allowing the contents to discharge; the pipette is then washed with three successive changes of water of 10 c.c. each, introduced through the funnel. The wash water spreads over the inner surface, removing every trace of reagent. The pipette is filled from the bottom and is worked automatically by a filter pump. The mounting and connection are shown in Chapter X under the title, "Determination of copper by electrolysis."

ELECTRICAL DATA

6. Normal Current Density, in the electrolytic deposition of metals, is stated as "*amperes per square decimeter*" (100 sq. cm.) of immersed cathode surface, counting both sides of the plate upon which the deposit is made.

7. Electrical power for the determinations by electrolysis is usually delivered as a direct dynamo current of 100–115 volts potential. If the current is only available by day, or is alternating, it is better to install a small motor-generator set or charge storage cells to deliver a current at 6 to 10 volts tension than to bother with inferior primary batteries. *Accumulators* with a capacity of 10 amperes and a voltage of 2.2 to 2.5 per cell cost about \$10 each. The current may be reduced by small ventilated rheostats, one of which is connected to each independent group of six pairs of electrode clamps. The wires leading to each set should be provided with a special switch connection to an ammeter and voltmeter. The first instrument may read up to 10, the latter to 5 units.

8. **Electrolytic Cabinets** are varied in design according to the work. The Tennessee and Cananea Companies use the Guess-Haultain cabinet, which is specially adapted to ore-testing, because the electrodes are made of very thin corrugated foil and sand-blasted.

A heavier equipment is required for the assay of metal. There are two systems in use for connecting the individual assays, or clamps, to the main wires from the generators. In the first system, represented by the rack of A. M. Smoot (Fig. 4), or the

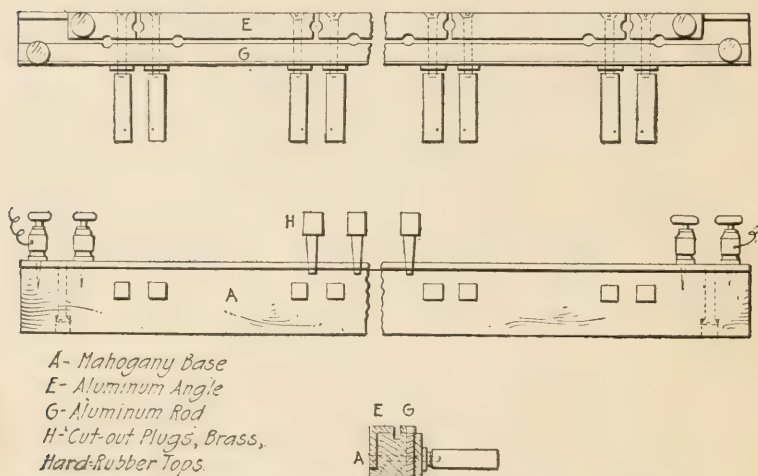


Fig. 4. — Rack for 10 Electrolyses in Series.

cabinet of E. Keller, the assays are arranged in *series*, and a plug must be inserted as each assay is withdrawn, to allow the current to pass.

In the second system, also in general use, the assays are arranged in small sets of five or six assays, in *parallel* connection. The withdrawal of any assay does not break the circuit, but causes the remaining assays to receive more current, temporarily.

(a) *Series System*. — Mr. Smoot has a special device to permit the rapid withdrawal of electrodes without breaking the circuit, or permitting the contacts, at any time, to mar the wires and alter their weight. There should be no exposed screws or brass connections liable to corrosion above the assay beakers. The simple form of rack, illustrated in Figs. 4, 5, 6, is arranged

to hold ten assays in series, the maximum number which may be placed on one wooden bar of this type, although any number of racks may be joined, according to the voltage of the available current. The details of the special rubber binding post are shown in Fig. 5.

The wires of the electrodes pass through the holes in the rubber caps and are held firmly in the V-shaped slots in the aluminum rods by the pressure of the springs, which tend always to push the caps to one side. An immediate release is effected simply by pushing the sides of the rubber caps against the springs. There are no wires, the current being carried through aluminum or brass rods of larger cross-section. All metal over the beakers is protected, the connections being shown in illustrations No. 5 and 6. The current of two cells is employed, although current from a dynamo, through two rheostats, may be used instead. The wires from

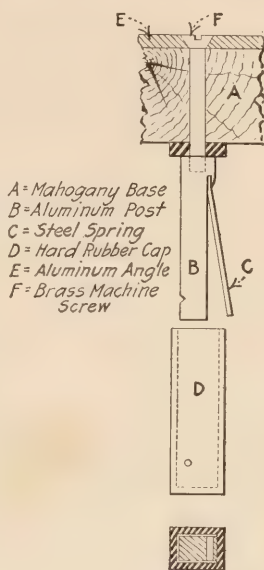


Fig. 5.—Plan of Binding Post.

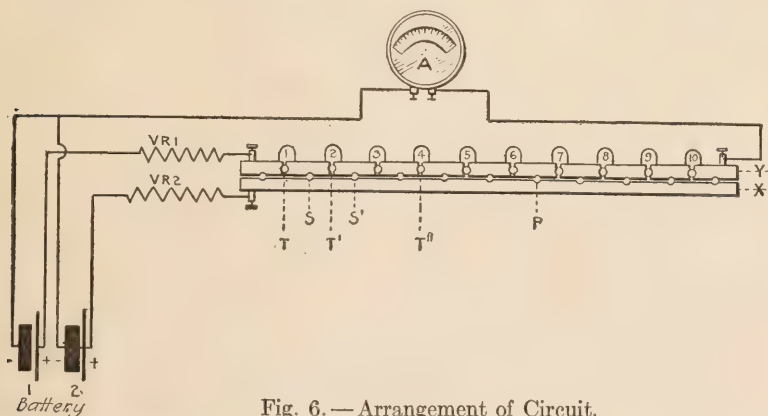


Fig. 6.—Arrangement of Circuit.

battery 1 pass through all assays. At point P, a plug is inserted connecting bar X with bar Y, and the variable resistance VR of battery 2 is regulated so that the ammeter A registers .40 amperes.

point "T," thus short-circuiting test No. 4, which may be withdrawn so quickly that no copper can redissolve.

(b) *The Parallel System*, with tests arranged in small groups, as adopted by the Calumet & Hecla Laboratories, and by the American Brass Co., seems to permit as rapid manipulation as any rack yet designed. In the C. & H. apparatus, brass terminals rest upon a continuous shelf of hard vulcanite — perforated with small holes just large enough for the electrode wires, so there is no chance for injurious corrosion of the terminals, which are soldered to the insulated leads. The electrode clamps are arranged in pairs on the long strip of vulcanite, or hard rubber, which is

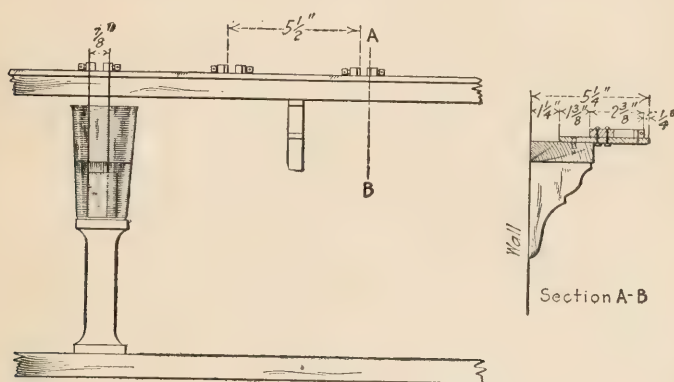


Fig. 8. — Rack for Electrolysis — *Parallel System*.

6.3 mm. thick and 10 cm. wide and is supported on brackets, with the under side of the strip 30 cm. above the main shelf. About six pairs of brass terminals are connected in parallel with two large copper wires which lead directly to an individual switch, rheostat, and ammeter switch. Assays may be taken off, one by one, without inserting any plugs, the current being gradually reduced after each removal, by means of the variable resistance. This system consumes a little more current than the first or series arrangement.

The electrode clamps are made from square brass rods, 1 cm. diameter and 5 cm. (2 inches) in length. A V-shaped slot is made on the rear end of each, and the conducting wire, with the insulation removed at this point only, is laid in the slot and soldered. It may be more convenient, in small installations, to

employ as variable resistances, small banks of incandescent lamp sockets, in which may be inserted lamps of varied candle power, or amperage. Storage accumulators are conveniently charged through lamps as resistances. Figs. 7 and 8 show the design. The beakers rest upon wooden spools. The manipulation of the assays is described in Chapter XI.

(c) *The European Equipment* of the Mansfeld Works merits a short description. According to Hermann Koch, a current at 3000 volts is reduced by a transformer and motor-generator to a 100 ampere current at 8 volts tension, which is used to charge

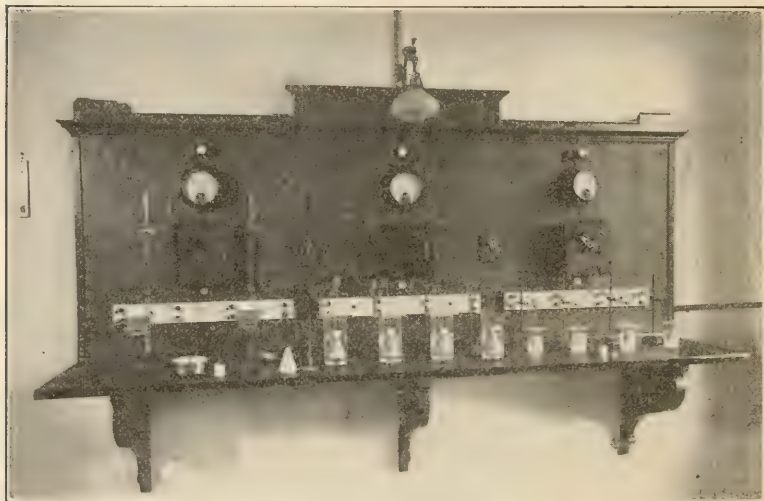


Fig. 9. — Mansfeld Electrolytic Table.

three large accumulators, furnishing ordinarily about 25 amperes for electrolysis at the present time.

Fig. 9 illustrates a special table for electrolysis.

The resistances, which reduce the tension to 2–2.8 volts for each assay, are iron frames with 12 bobbins. Special connections give equal tension at all electrodes, independent of changes in total load. The ampere meters read up to 5 amperes for each group of 3 to 16 assays. For the final division of the current (.1–.5 ampere per assay), small marble slabs are fastened to the back board, bearing two rows of brass connectors which carry the current to the positive and negative clamps and tripods. The American Brass Co. use a double system of conducting

metal posts, of similar design, but connected below the table, so that the wiring is concealed. A rheostat is provided for each group of five assays.

DEVICES FOR THE CIRCULATION OF ELECTROLYTES

9. Systems in General Use. — 1st. Rotation of the anode, or cathode, by attachment to a spindle driven at high speed by a small electric motor. 2d. Rotation of the solution in the beaker by electro-magnetic force, as in the "Rotary Device" of Professor F. C. Frary.¹ (W. B. Price has obtained good circulation in brass analysis, by blowing compressed air upward through a small tube near the anode.)

For the first system, a good anode may be made from a stout platinum wire to the bottom of which is clamped a round bladed propeller, 2.5 cm. in diameter. According to the inventor,² the Frary Solenoid, or "Rotary Device," has been patented only in Germany, but can be obtained from the Vereinigten Fabriken für Laboratoriums-Bedarf, Berlin, — or their agents, the Standard Scientific Co., New York:

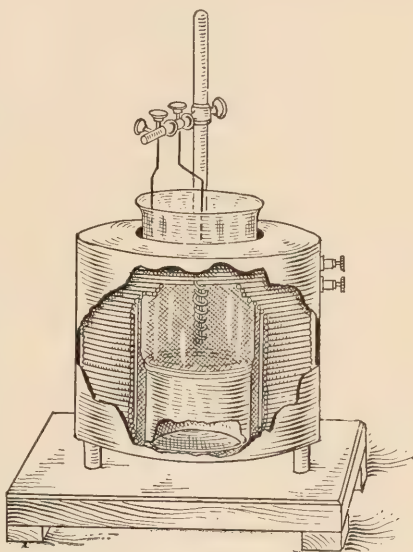


Fig. 10a. — Frary Rotary Device.

Fig. 10a illustrates this model, and 10b shows a modification which the author was obliged to devise some years ago (before Professor Frary's paper had been noted), in order to accommodate a beaker 12.5 cm. high and 5.7 cm. diameter. A large size was designed to accommodate a No. 5 (750 c.c.) beaker, and provided with small tubes to conduct cold water between the beaker and the copper cylinder surrounding it. The copper cylinder is brazed water-tight to an upper and lower plate of soft steel,

¹ *Z. Electrochem.*, 13 (1907), 308.

² Letter.

forming a reel, which is coated with mica and wound with about 500 turns of No. 13 (B. & S. gauge) insulated copper wire.¹

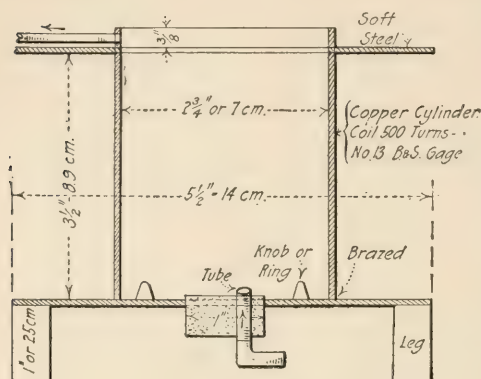


Fig. 10b. — Sectional View of Water-cooled Solenoid.

The electric current is usually passed through the electrodes and coil in series. A magnetic field is produced in the solution which constantly diverts the lines of force passing radially from anode to cathode. With the largest size of apparatus, the author uses a cathode cylinder of platinum sheet, 7.5 diameter, 11 cm. high, and perforated with holes 3 mm. diameter, spaced 1 cm. apart.

EQUIPMENT FOR DRILLING OF CAST COPPER

10. Strong power drills must be used generally, and it is convenient to have one with a gauge on the vertical spindle. Small direct-connected electric drills are sometimes employed for gold and silver bullion.

For ingots and the thin square plates recommended by Edward Keller for argentiferous metal (Chapter II), the author uses boxes 15 cm. in depth, made from $\frac{1}{16}$ -inch sheet steel, to preserve all the chips from the drill. The drill should be free from all traces of oil. The ingots, etc., are easily held in place by large flat wedges, and the square plates are supported by shoulder pieces brazed to the bottom sheet, inside the box.

WEIGHTS

11. **Standard Weights.** — In regard to this matter, the author cannot too strongly recommend that all large laboratories preserve as a reference standard, a special gold-plated set of double-checked weights from 100 g. to 1 mg., to which the weights of all other balances shall be periodically adjusted by the method of substitution.

¹ *J. Ind. and Eng. C.* 3 (1911).

For the daily weighing of the five-gram samples of refined copper, F. D. Greenwood employs a special five-gram brass weight, which is again placed on the balance in taking the weight of the electrode and deposited copper. This brings the total deficiency, or difference from the original weight of copper, on the milligram weights and rider (see Chapter XI).

CHAPTER II

SAMPLING AND CRUSHING

Treatment of the Subject. — A number of the best mining experts have recorded their testimony to the fact that faulty sampling has been the cause of greater disagreement and losses than any inherent defect in the assay methods usually employed or any personal equation in their operation. For the mathematical theory of the subject, any one may consult the exhaustive papers of D. W. Brunton (1) and S. A. Reed (2) on ores, and E. F. Keller for metallic copper (2*b*). Only the regular practice of mines and metallurgical works will be considered in this chapter (3). Whatever plan is locally adopted, it should furnish good agreement between contracting parties and, where samples are taken throughout the various mining and smelting operations of any company, the sampling should be done with such care that a full exhibit may be made of the absolute and relative gains, or losses, of the successive operations of ore and metal treatment.

Divisions of the Subject. — 1. Mines. 2. Western sampling mills. 3. Stamp mill control. 4. Carload lots of ores at eastern smelters. 5. Slags and copper products within the smelting works.

DIVISION 1 — MINE SAMPLING

1. In the valuation of prospects and control of mines by sampling and assaying there are three general systems. For a full description several papers are listed at the end of the chapter where all the references are tabulated. The general opinion of the best authorities is made the basis of the directions outlined.

System A. — The selection of a large number of small samples, cut quickly across the vein, at points evenly placed in parallel lines across the whole area, as exposed. The first, and least expensive, system gives correct results only on soft ores of uniform grade and is used for testing new stopes, etc., in producing mines of uniform character. The grooves are made about 3

inches (7.5 cm.) in width and 6 inches deep in soft ores or about 1 inch deep in quartz, and finally trimmed to uniform size.

System B.—A smaller number of heavy samples, at equal distances but farther apart, and large enough, if blasting of grooves is absolutely necessary, to represent all the variations along the lines of cutting. Such a sample, in operating properties, may weigh from 25 to 50 tons to represent a stope, although with new properties, the usual amount is 50 to 400 pounds (Kirby). Philip Argall assumes 5 pounds per foot across 10 feet of vein, or stope. This system is advisable for all American hard ores, where the values are very uneven and is the most frequently employed for accurate valuation.

System C consists of actual "mill runs" of lots of 50 tons, and more, of regularly mined ore from each stope, or chute. The sample may be cut out by mechanical sampling mill after the ore has left the mine. Such a large works sample is necessary for native copper (see description by C. H. Benedict [7]). Even such tests may be deceptive with regard to the quality of ore that can be regularly produced.

2. Practical Notes.—These are based on papers of E. P. Mathewson, D. W. Brunton, and others. Ordinary duck, etc., will catch wire gold, or copper metal. The best cloth to use for mine rock, where the pieces are small, is soft flexible enameled oil cloth. Samples of over one ton, and made up of pieces at least three inches in diameter, may be reduced at the mine to one ton by throwing aside every tenth shovel, if the work must be done by hand. Such fractions are then reduced to one-half inch size, and five to fifty pounds weight, by crushing and dividing.

A hammer tends to break off hard projections, while a geologist's hammer seeks the soft spots; hence the best tool, in the opinion of many experts, is a moil struck by a four-pound hammer.

The sampling stations should be tied to the survey stations on the mine maps to permit re-sampling. A conservative definition of the phrase "ore developed" is that it means ore exposed on four sides.

METHODS AT THE MANSFELD MINES

3. At Mines.—The largest mines of Germany still find, after eighty years' experience, that the *first system*, *A* is best

suited to their conditions. A description of the system, by H. Koch, has been necessarily condensed in translation. The sampling of the hoisted ore (including the mineral typolite and shales from the quarries) is carried out at both the shafts and the smelter, so that the same smelting stock is examined twice. The necessity for this procedure arises from the exceedingly variable nature of the slates. Only an average result of the metallic contents of the doubled samples can be considered accurate, although the metal can be closely determined in each one as received. The samples at the shafts are taken by small scoops or troughs out of the mine cars or cable-buckets, while they are being filled, and in such proportion that the total weight of sample amounts to nearly $\frac{1}{200}$ of the ore hoisted.

The material, keeping that from the quarries and mines separate, is united to form daily catch samples from each shaft, stamped or crushed in machines, pulverized, sifted, well mixed, reduced to about one hundred grams, and then examined by color test to assign its grade as to copper (assay weight, 2 g.). From the same samples, one gram is taken (for each metric ton loaded), to form a weekly catch sample, which again is reduced, mixed and graded as to copper contents by the colorimetric test; then delivered to the central laboratory, where the accurate determination of the copper and silver is completed by electrolysis and cupellation.

4. At the Smelting Works, samples are taken during the discharge of the ore cars from the mines, and are collected separately from each shaft or quarry to constitute daily quarry and mine samples, which are ground down as at the mines and tested colorimetrically. For each ton of ore received one gram is reserved for a monthly sample, and this material, after proper mixing and reduction, is tested by color test at the mines, and by gravimetric analysis at the smelter.

The values obtained from the monthly average samples taken at the smelter are compared with the monthly averages computed from the weekly average test samples taken at the shafts. The arithmetical mean of the mine and smelter samples is taken as the basis of the office reports. To judge of the (probable) values, frequent tests are also made of gossan, and surface strata, and assayed partly by color at the mine, partly for copper and silver at the main laboratory.

Raw Ore from Smelting Ore-beds. — When a stream of ore is cut out of the bedding-pile, 9 to 10 spoon samples are taken (5 to 6 from each cut of 7 metric tons), and collected as one sample until 25 tons are smelted. This average unit sample (reduced to about 200 g.) goes to the laboratory for the valuation of the copper and silver contents.

From the finished samples, a monthly average sample is made up for complete analysis.

DIVISION 2 — MECHANICAL SAMPLING

5. The daily control of the large western mines is effected by diverting a fixed proportion of the daily product of the mine (perhaps one-tenth of the cars if the ore is uniform) to a sampling mill, located at the smelter, or at the mill if the ore requires concentration.

At the Anaconda Mines, Montana, the sample lots of ore are elevated to bins at the top of the sampling building, and then passed down through an alternating succession of rolls, crushers, and four Vezin samplers until the ore is cut to a portion of 3.2 pounds for each ton of the original sample. $\frac{1}{5} \times \frac{1}{5} \times \frac{1}{5} \times \frac{1}{5} = \frac{1}{625}$ and $\frac{1}{625} \times 2000 = 3.2$. The new five-story mill of the Calumet & Arizona will reduce a ton by four Snyder machines to 1.6 or 3.2 pounds, according to the nature of the ore sampled.

The product of the mechanical samplers is further reduced on an iron floor by Brunton shovels. The Garfield smelter is said to reduce the ore by causing the sample to be heaped into cones which are flattened and divided by iron crosses against which the material is shoveled. These crosses are made, in several sizes, from $10 \times \frac{1}{16}$ inch iron plates of suitable lengths, set vertically. (A short discussion of the requirements of a good sampler, and of Eastern practice, is given in 13, Division 4.)

When the sample is reduced to 100 or even 25 pounds (varying with the locality) the ore is dried on a steam drier to determine the moisture, and the dry material put through an Engelhardt sample grinder, divided by riffles, bucked to pass a 100-mesh sieve (100 to the linear inch), and put in four packages of 6 to 12 ounces each. One goes to the laboratory, one to the owner of the ore, and two are filed away in case of dispute. In some works the product of the last machine, reduced to 100 or even 25 pounds,

goes direct to the laboratory for all the further reduction and moisture test. There it is ground, quartered, and riffled down to about 50 ounces by a fixed rule, which must be the result of experiment with different classes of ores. The rule actually depends on the principle, that during the reduction of the ore by grinding, sifting, and quartering, there is in each successive product a fixed ratio of the largest particles of valuable metal, or sulphides, to the whole weight of each size which must not be exceeded or the final error will be too great, i.e., quartering must not be carried too far, before grinding finer. The separation of the fine and coarse particles in transit through the modern mechanical sampling mill is taken care of satisfactorily by reducing the length of the spouts between cutting devices, and using a shaking feed for all crushers and rolls. Any metallics on the sieves are weighed along with the ore portion from which they were taken and separately assayed, unless they can be ground in with the ore by passing through the grinder a second time.

IRON FROM GRINDING PLATES

6. **Iron** is introduced into all hard ores, when finely pulverized by steel plates. In furnace slags, the iron derived from wear may amount to 0.3 per cent. To make a correction factor, pass some of each class of material through crusher, and reduce in large porcelain mortar, and agate, or Abbe ball mill. Compare the iron in this sample with the other.

DIVISION 3—SAMPLING IN STAMP MILLS

7. Concentrates in Western mills are passed through mechanical samplers. The following description by C. H. Benedict, of the sampling in the Calumet & Hecla Stamp Mills, illustrates a correct principle, adapted to the study and control of milling operations in any district.

There is no custom milling, as generally accepted, on Lake Superior. A mine without a mill leases the exclusive use of one or more stamp heads and owns the product. In this way, there is no necessity of sampling mills, if, in fact, the nature of the rock made such sampling possible. The quality of the rock is found by adding the assay value of the concentrates to that of the tailings.

In order to test out a given milling process, however, tests are frequently made by taking samples of all products for a week on amygdaloid (or if on conglomerate rock, about four days),

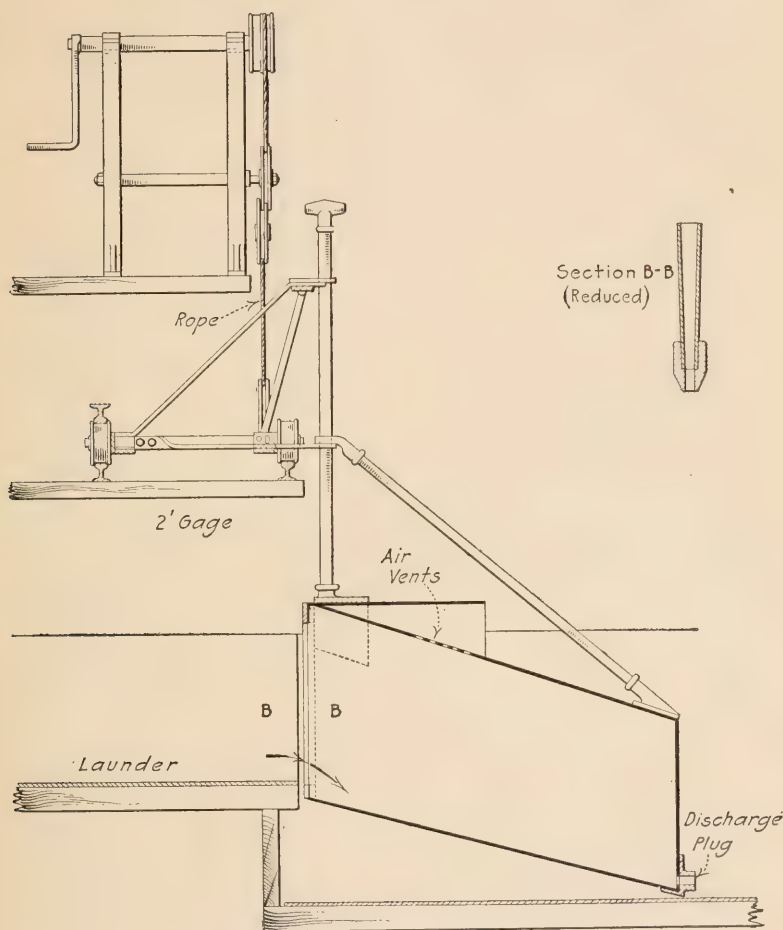


Fig. 11.—Sampler for Mill Tailings.

in order to get the variations in stamping. During such tests, samples are ordinarily taken of each product for *one* second every hour. For the overflow of jigs, the sampler makes use of a long shallow iron trough, "U" shaped, and a little longer than the width of the jig, holding the trough cross-wise under the whole stream

for the time specified. "From these time samples, the calculated tonnage must, of course, check closely with the car weights of the rock, originally stamped." Concentrates are weighed in bulk and tested in one of two ways — by means of a slotted sampling pipe — or by the "spoon and shovel." In the first case, a $\frac{3}{4}$ -inch (1.9 cm.) pipe (with a slot cut out in the side and one edge faced out to make a projecting lip) is driven into the car of wet mineral, the pipe turned, and the resulting sample shaken out into long pans. In the second method, a portion is taken by a spoon, or similar device, from a shovelful, at regular intervals. Middlings are sampled in the same way as the tailings.

8. Tailings of the Calumet & Hecla Mining Co. are all elevated by sand wheels and leave the mill in a launder 54 inches (1.37 m.) wide, and with a stream about 8 inches deep. A sample from this launder is taken every hour and a half, day and night, by means of the slotted sampling machine shown in Fig. 11.

This sampler consists essentially of a fan-shaped receptacle with a slotted end, which is carried through the stream by being suspended on a track over the stream (and is afterward hoisted by the spindle, in order to discharge it over the edge of the launder into a metal barrel). The samples from each shift are then combined, and should be dried in large tarred pans over steam coils, then screened through a succession of sieves (of 10, 20, 40, and 60 meshes to the linear inch). The resulting fine products are weighed, sampled, and the calculated assay from the sizings checked up against the original assay.

Laboratory reduction of these samples of tailings, or mineral, is accomplished ordinarily by permitting the dried sample, if large, to flow through a hopper, and cutting the resulting stream of dry pulp with a rectangular pan, moving in time with a pendulum. If the sample is small it is poured through a funnel, held in the hand over cut-out riffles.

The size of the sample for the assayer is regulated by the coarseness of the material, and is usually about 40 grams. This is crushed through a 60-mesh sieve, the resulting metallics picked out to constitute a separate sample, and the fines reduced to portions of 5 grams for electrolytic assay. The combined assay values of *tailings* from the different machines must check with the assay of the *general tailings* from the main waste launder.

DIVISION 4—SAMPLING AT REFINERIES

9. Mill concentrates of native copper are sampled in the refinery from hand carts, or from chutes, when weighed out to the furnaces, taking say two small cups for each thousand pounds of the wet product.

The daily samples from each grade, and from each mine, are kept in water-tight copper cans, inclosed in a water-tight wooden box, until the percentage of water and copper can be determined.

At Custom Sampling Works, New York (By A. M. Smoot). — There should be no invariable rules for the sampling of copper ores and mattes, because, while the grade and physical condition are the principal factors in determining the procedure, varying conditions of sale and delivery must also be considered.

10. Hand Sampling. — Low-grade copper ores, containing only small amounts of gold and silver, may be conveniently tested in 100-ton lots. If the ore shows no pieces larger than 4 inches (10 cm.) diameter, take every tenth barrowful as it is discharged from cars, or every tenth bucketful as it is taken from vessels, and set it aside for a sample.

Crush the 10 per cent sample to 2-inch size, or 5 cm. diameter, and by half shoveling, reduce it to five tons (or 4536 kg.). Crush this to 1 inch (2.5 cm.) diameter, and reduce it again by half shoveling to one and a quarter tons. Crush to $\frac{1}{2}$ inch and reduce by shovel to 625 pounds (284 kilos). Crush to $\frac{1}{4}$ inch (or 4.2 mm.) diameter, and reduce by half shoveling, or preferably by riffing, to about 80 pounds (36 kilos), crush to pass a sieve of 16 meshes to the linear inch and reduce by riffing to about five pounds (2.3 kilos). Reduce this to pass an 80- or 100-mesh sieve, mix well, and divide by riffing into the required number of sample packages. Quartering should be avoided, since it may easily lead to errors which will tend constantly in one direction. It is more laborious and costly than *half shoveling*.

11. Rich Ores, containing appreciable gold and silver values, as well as high copper, should be divided into fifty or even twenty-five ton lots (22.7 metric tons) for sampling, unless they are very uniform. If possible, all rich ores should be crushed to 2 inches (5 cm.) diameter before any division is attempted. Take every fifth shovelful as a sample, crush to $\frac{3}{4}$ inch (1.9 cm.), and reduce by half shoveling to $2\frac{1}{2}$ tons, crush to $\frac{1}{4}$ inch (6.3 mm.), and reduce to

five hundred pounds, crush to pass eight meshes to the linear inch and reduce to fifty pounds; then crush to pass 20 mesh and reduce to five pounds (2.27 kilos). Grind this through a 100-mesh sieve (39 meshes per cm.), mix well, and divide into the required number of assay samples.

12. Mattes. — These are sampled like rich ores, but some material with high gold and silver values will require finer crushing throughout and more intimate mixing between the reductions. See note on western methods.

Duplicate samples of such rich mattes should be taken from the very beginning of the operations. Duplicates, which are made by dividing a single sample at some point toward the end of the coarse crushing, only serve to check the final work. Duplicates are especially desirable with very variable material; for instance, where two or three small lots of widely different character are to be sampled as one lot. In such cases as this all of the material should be crushed to at least $\frac{3}{4}$ inch (1.9 cm.), and mixed by coning before any subdivision is attempted.

Fine crushing throughout. — It is the practice at some eastern works to crush the whole ten or twenty per cent sample from the original lot to $\frac{1}{4}$ inch (6.3 mm.), and then by repeated mixing and half-shoveling to reduce it at once, without further crushing, to 250 or 300 pounds. This is done on the ground that it is cheaper to crush the whole sample than to introduce several intermediate samples of coarser materials.

The crushing of the whole lot is insisted upon by one or two western plants, when a car is loaded with a mixture of reverberatory and cupola furnace mattes. Although a satisfactory sample is obtained, the production of a large amount of fines is often objectionable to the smelter. If care is used throughout in hand sampling, the results are accurate, but treatment of large lots is too slow and costly.

NOTE. — Western *mechanical* practice has been outlined under Division 2.

13. Machine Sampling. — For large lots of uniform material, machines are more economical and practicable, as stated in the account of the systems of the western reduction works. The observation of several important points in construction and operation (which were not mentioned under mill practice) is essential to good

work. The sampler should be constructed so that the scoops or diverters cut the *whole* ore stream at frequent intervals. The scoops should permit a free fall to the stream after it is cut out, so that it shall not be retarded and so no pieces shall bounce outside. The openings in the scoops or diverters should be at right angles to the ore stream, and they should move across it with uniform speed, and at uniform intervals. The openings should be at least four times the diameter of the largest pieces which pass through them.

In machines such as the Vezin, in which the sample scoops revolve around a shaft, the shape of the scoops should be sectors of a circle whose center is the center of the shaft. The feed to the machine and the flow of the ore should be constant and uniform. The whole apparatus should be housed to prevent the escape of dust, and at the same time all parts should be easily accessible. As in western mills, the final product of the machine sampler passes to a closed box, or car, from which it is taken to a sampling floor and finished by hand. Ordinarily 50 tons would be cut by three machines to 800 pounds. The last machine sample would then be cut with a Jones riffle to 400 pounds, crushed to 12 mesh, and riffled to 50 pounds. Finally, crush to 20 mesh and riffle to 5 pounds, grind this to 100-mesh sieve, mix and divide it into the required number of samples.

14. Moisture Samples.—This question is very important, especially in ores. Since all ores and mattes are assayed on the dry basis and settlement is based on the dry weight, moisture samples should be taken at the time of weighing. Weighing is generally done immediately before sampling. For a moisture sample, at least 10 kilograms of ore should be taken after crushing to at least one-half inch, or preferably finer, but too much crushing should be avoided. The reject from the third mechanical crushing of the general sample usually affords a good moisture sample. Small moisture samples are useless.

DIVISION 5—FURNACE PRODUCTS

15. Reverberatory Slags.—Waste ore slags from matting furnaces can be taken at the door, or sluice, about once in 2 hours, or when skimming. Mineral slags from native copper contain 15–20 per cent of copper as silicate and shot metal and the last refining slags are full of carbon, so that the best average is ob-

tained by breaking all, or a half at least, of the cooled cakes from the slag buggies and taking pieces of equal size from the top, middle, and bottom of each block broken.

16. Matte in Western Works.— Small hand-ladles can be filled at the settler or hot metal ladle while tapping, or pieces can be taken by shoveling from the cool material, after crushing, if it is to be bagged for direct shipment. As already noted, some experts advise a preliminary fine crushing of the whole, in the case of a car of mixed reverberatory and cupola matte.

17. Cupola Waste Slags.— The method, sometimes adopted, of dipping an iron rod in the slag stream, and chilling it in water, does not show the average amount of shots of metal, or prills of matte. To secure an average sample, a small hand-ladle should be held under the full slag stream, and the contents quickly granulated with water in an iron pail, kept in a safe place. At Lake Superior, samples are taken once an hour and combined into one sample for each working shift.

18. Anode Slags (H. D. Greenwood).— The small slag pots are dumped and the shells cooled with water, which will help to disintegrate the large pieces. The large pieces are then broken up with hammers and sent through the crushers, where they are crushed to one-half, or one inch, pieces, all metallics being returned to the furnaces. The sample is coned and worked down by hand to about 200 pounds (or 90.7 kilos); then crushed finer and worked down to a laboratory sample, recrushing finer with each division. The metallics of each quartering are kept separate (as in the case of Lake Superior slags), and sampled, assayed, and proportioned accordingly.

19. Sampling of Molten Copper.— Edward Keller and others have proved that the difficulty of sampling pigs and other irregular deep castings at anode furnaces is eliminated, if thin square plates are cast with a full hot ladle directly from the molten charge, after it is well mixed and ready to pour into molds. Keller¹ recommended that a plate, 15 inches square by one inch in thickness, should be taken from the middle of each third of the charge as it was tapped from the furnace. With refined native copper, it has been proved that plates $6 \times 6 \times \frac{1}{2}$ inch are large enough. A uniform number of holes should be drilled through each plate, but the sampler should keep away from the edges for a distance

¹ *Trans. A. I. M. E.* 27 (1897), 106.

equal to twice the thickness of the plate, at least. A granulated shot sample, or one of the thin plates, may be correct for gold and silver if all skulling is avoided by pouring from a hot clean ladle. Keller insists that large shot samples should be re-melted, if variable, and a sample cast or granulated. The copper percentage, when determined upon the shot, cannot be as good an average of a lot as a result obtained from the plates, owing to the absence of some surface oxides which should be included in this case.

Superintendent William Wraith, of the Washoe Smelter, concluded, after many tests, that the pouring of shot from a hand-ladle tends to give high results for silver. His statement follows:¹

"The only method of furnace sampling which uniformly checks results obtained by drilling every fourth anode by a 99-hole template system consists in batting out samples from the molten stream of metal, while pouring, and allowing the copper to fall into water.

"The first sample is batted from the stream with a wooden paddle, 30 minutes after starting to pour, three other samples being taken at one-hour intervals, each portion weighing from 4 to 6 ounces. These samples are dried, examined for burnt wood, screened on a 10-mesh screen of No. 8 wire, to remove fines, the oversize then screened on a 4-mesh screen of No. 20 wire, to remove the coarse, the undersize of this screen being taken as the sample. The four portions are thoroughly mixed, and split in half by passing over a 16-slot splitting device, slots being 0.5 inch wide, one-half being kept as a reserve sample, and one-half assayed."

SLABS AND ANODES

20. (From A. M. Smoot, F. Andrews, and H. D. Greenwood.)
—The method of A. M. Smoot, for the custom sampling of pig copper and anodes, is presented first, as it gives a full explanation of the reasons for every step taken by the large refineries in this rather difficult problem. Nearly all custom refineries adopt the same principle.

The *template system* of sampling takes into account the segregation of the constituents which occur when any molten alloy is cast into a mold and chilled. The word "bar," as used here, includes any commercial shapes into which crude copper is cast for shipment. By this system, the top and bottom surfaces of any given bar, cake, or slab are divided into a number of squares, each of which is a bounding surface either of a parallelepipedon or a wedge. By drilling holes in the centers of these squares,

¹ *Trans. A. I. M. E.* 41 (1910), 318.

clear through the bars, borings representing the contents of the solid figures are obtained. By making the squares small and drilling a large number of holes in rotation, an accurate sample representing the metallic contents of any given bar may be obtained. An accurate sample of the lot may be obtained by taking a large number of bars of the same shape and character, and drilling successive holes, one in each bar, each corresponding in position to one of a series of squares marked off on the top of a single bar, that is, by advancing the drill one hole in the template with each successive bar. The number of bars taken to represent a lot should depend on the number of bars in the lot and on the character and tenor of the crude copper. In shipments made up of several converter charges of varying gold and silver contents, all of the bars should be drilled.

When the material is of nearly even composition, such as the product of a smelter handling uniform ore from a single mine or district, a smaller proportion (for instance one-fourth or even one-tenth) of the bars will represent the lot. In sampling copper which is high in gold and silver, even when it is of fairly uniform grade, every bar should be drilled. When a fraction of the number of bars in a lot is taken, the number should correspond with the number of holes in the template or to some even multiple of this number, so that one or more complete cycles shall be used and every hole in the template be represented in the sample. This is not important where a number of successive lots of the same material are sampled. In such cases, the rotation of drill holes may overlap from one lot to the next. (Refer to Andrews's account.)

Since segregation on cooling takes place quite uniformly from or towards every cooling surface, a quarter or half a bar may be assumed to contain all the elements of segregation and a quarter or half section template may be used. This is advantageous because a larger number of small squares may be laid out on the smaller templates, and still keep the same number of holes within the number of bars to be drilled. In drilling bars with a flange or wedge, the template should be laid out so that the weight of borings from the wedge-shaped part of the bar is in the same ratio to that taken from the rectangular part as the weight of the wedge portion is to the weight of the rectangular portion. All holes are usually drilled with a half-inch (1.27 cm.) drill, and must

extend clear through the bar. Too much emphasis cannot be laid on this point. The drill should be driven at high speed with a light feed, so that the drillings may be thin and easily ground. Forcing the drill produces thick drillings.

The top surface of crude copper is usually very rough from the escape of gases, especially in the central portion. The top surfaces at the edges are usually fairly smooth. The rough top surface frequently contains undecomposed matte and sometimes small pieces of slag, as also an excess of cuprous oxide. As cuprous oxide is a solvent for silver, the top skin of crude copper bars is frequently higher in silver than the underlying metal. It is, of course, poorer in copper.

In drilling bars with the top surface up — or towards — the drill, some of the smaller particles of the borings become lost in the interstices of the rough surface; they cannot be completely collected. The smaller particles consist in part of the brittle top surface; thus drillings from rough bars made with the *top* surface up are not an average sample. When bars are drilled with the *bottom* surface up, the pressure of the drill is apt to break off rather large pieces, forming craters in the brittle crust when the drill is thrust through the bar. It is, therefore, customary to drill half of the sample bars with the tops of the bars up and half in the reverse position. The drill holes in the wedge must necessarily be taken with the top of the bar uppermost.

Shipment of Samples.— Containers for powdered ore or drillings of crude copper usually consist of sacks, stout manila paper bags, or printed envelopes with patent fasteners. Drillings of refined copper should, however, always be kept in tight glass-stoppered bottles and shipped in capped bottles in special mailing cases to provide absolute protection from oxidation in transit.

21. Reduction to Assay Sample.— The weight of drillings from the usual shipping lots may be twenty to thirty pounds (9 to 14 kilos). All drillings must be ground and mixed before division. The grinding is done in a mill with slightly corrugated or toothed plates. The movable plate revolves horizontally against the fixed plate. They may be of good cast iron, but chrome steel is better, although it is difficult to get good castings of this material and inequalities cannot be adjusted by machining.

All the drillings should be ground to pass a screen with 8 meshes to the linear inch, and then thoroughly mixed and divided

on a riffle, or split sampler, to obtain a sample of seven or eight pounds (3.2 to 3.7 kilos). This sample should be ground repeatedly, until all particles pass at least a 16-mesh screen. A fineness of 20 mesh is preferable and drillings may easily be ground to this fineness if they are thin enough originally. The finely ground drillings should be thoroughly mixed and divided with a split sampler or riffle into the required number of packages. No attempt should be made to dip with a spatula, or to quarter the ground borings, but the greatest care must be used to include the proper proportion of fine and coarse in each package.

If much gold and silver are present and there is a large difference between the assay values of the fine and coarse parts of the ground sample, the whole of the 16- or 20-mesh sample should be weighed and separated into fines and coarse on a screen of 40 meshes to the linear inch. The fines should be weighed and the finished samples should include separate parcels of the coarse and the fine parts together with a memorandum of weights and their mutual ratio.

22. Method of F. Andrews. — The principle given is the same as the one first quoted. This system provides for material of *variable* composition.

From 20 to 100 per cent of the lot is sampled by drilling a $\frac{1}{2}$ -inch hole through each sample piece, and in rotation as already directed. The templates are of the exact size of the surface to be covered, and each brand of material has, of course, its own independent template. The drillings are ground twice and then cut down by a divider to four or five pounds. This amount is then further ground until it all passes through a 16-mesh sieve. The whole sample is then put through a 40-mesh sieve, the coarse and fines weighed, and the required number of samples put up with proportionate parts of coarse and fines in separate bags.

Each sample then comes to the laboratory composed of two parts, one (coarse) which has remained on the 40-mesh sieve and the other (fine) which has passed through. In weighing up for the gold-silver assay, the assay ton is made up of proportionate parts of coarse and fines, but the copper assay is made on each part separately, 5-gram portions being used and the correct assay figured from the proper weights.

23. Method of F. D. Greenwood (for uniform material). — It is recommended that the ground borings should be directly cut

down on a split sampler in such a way as to obtain a sample of about 1 assay ton (29.167 grams) for the gold or silver assay. For the copper assay of crude bullion, 80 grams are taken, and in each case the final sample must include the proper proportion of the finer and coarser parts of the borings.

This sample must be very carefully obtained for reasons already stated. Portions "dipped" from the sample bottle or from the sample spread out on paper, are likely to contain undue amounts of coarse or fine.

24. Metallic Iron in Drillings (A. M. Smoot). — There is a very small amount of iron introduced in the drilling and grinding of converter and blister copper, but it is wrong to attempt to remove it from the ground borings by a magnet, because crude copper always contains magnetic particles, due to matte, etc., which properly belong to the sample. Any attempt to remove such iron with a magnet will introduce a larger error than it will cure. Practically, the amount of iron derived from the tools is negligible, since ground turnings seldom contain more than .03 per cent, and a large part of this is present in the original copper.

Iron due to the tools may be separated in part by treating the original turnings with a magnet and carefully saving the magnetic particles. After grinding in the mill and dividing by riffle to the amount required for the sample packages, go over the drillings again with a magnet and discard any magnetic particles obtained. Restore to the sample a proportionate part of the magnetic particles originally found in the whole sample and mix thoroughly.

25. Moisture in Converter and Blister Copper. — The rough surface of such metal contains many cavities which may retain appreciable moisture if the copper has been exposed to the weather. This is apt to occur in winter when bars have been stored in yards exposed to snow, or shipped without protective covering. The per cent of superficial moisture is, of course, very small, and the average amount may be easily ascertained by moderate drying.

Bosh-cooled crude copper nearly always contains "occluded" water held in large cavities under the rough surfaces which could not be affected by weather. The "occluded moisture" may in some cases amount to 0.1 per cent or even 0.2 per cent by weight. This moisture is difficult to remove. Long continued drying at a temperature of about 350° F. is necessary. Of course, such

moisture is unevenly distributed, and a large number of bars must be dried to secure even reasonable accuracy. This necessitates a special drying chamber.

SAMPLING OF REFINED WIRE-BARS, CAKES, AND INGOTS

26. The method specified by the American Society for Testing Materials in the year 1913, for drilling cast metal, involves the driving of several holes clear through the casting in three directions, from top, side, and bottom, after removing and rejecting the surface oxide from the space drilled.

F. D. Greenwood, and others, drill the holes $\frac{1}{8}$ inch to $\frac{1}{4}$ inch deep, rejecting the drillings, then drill in the same holes until the drill is within $\frac{1}{4}$ inch from the bottom. The drillings are cut up with snips and only clean bright drillings are accepted.

The author drills two holes, at least, in the top, side, and bottom, with the precautions specified, but only halfway through, which gives practically the same sample but causes less heating and danger of oxidation. All borings must be tested with a magnet and freed from dirt by sifting through a 40-mesh sieve, then placed in clean dry bottles, as they oxidize rapidly if stored, or shipped, in envelopes. Flat anodes or sample plates are drilled through, including the oxide, as indicated under "The sampling of molten copper at furnaces."

SAMPLING OF COAL AT SMELTING WORKS

A special system is recommended for the sampling of cars and cargoes. The methods of subsequent reduction are those proposed by a joint committee of the American Society for Testing Materials and the American Chemical Society, and published jointly during 1914.

27. **Shipment of Samples.** — If samples are shipped from a distance, much moisture will be lost unless the containers are sealed. When the moisture content is important, the sample should be broken to half-inch size as accumulated, the mixing done quickly, and the sample transferred to a glass fruit jar or tin with screw cap, which may be made air-tight by sealing with adhesive rubber tape and gaskets. Three pounds is a usual sample for long-distance shipment.

28. **Car Sampling.** — The 1899 Coal Committee¹ recom-

¹ *J. Am. Chem. Soc.* (1899), 1116. See also "Coal," by Sommermeier.

mended that the sampler should take a sample of six scoop shovels at regular intervals on each side of the car. The shovel should be brought out full. Spread on a tight floor and break all lumps larger than an orange. Shovel, quarter, break finer (in a power crusher if possible), and quarter or riffle until the sample is reduced to 3 pounds. Manipulate quickly and transfer to a large fruit jar. A carload of such material as lignite may lose several hundred pounds in transit, and the U. S. Geological Survey has proved that during a 150-mile haul, there is a decided tendency for slate to settle. In such a case, sample the whole face of the load at the middle and ends of the car, while unloading.

According to A. D. Little, the ratio of the largest pieces of coal to the total weight of sample at each stage of the reduction process should be less than 0.01 per cent, if errors of 1 per cent in the ash determination are not to be exceeded in a single sampling of a fuel containing 5 per cent of ash. N. W. Lord insists that this ratio should be that of the maximum slate sizes to the total sample, which is a good proviso for very low-grade fuel.¹

29. Vessel Cargoes. — To sample coal on a very large scale, as unloaded by several power hoists, the system adopted by the Calumet & Hecla Mining Co. is recommended. A large covered barrel of corrugated galvanized iron is placed beside the scales on the elevated platform of each hoist. The buckets of coal are dumped on a grizzly, or coarse screen, from which the clean lump coal flows to the gravity distributing car. The weigher grabs a piece of coal (without selection) from one car out of five, or in such proportion that the total sample shall be about one part in five thousand.

The *fine coal* slides beneath the hoist down a closed chute, from which it is drawn into railroad cars and sent to boilers for immediate consumption. The fines are separately weighed, sampled, and analyzed. The analysis of the whole cargo is then calculated from the tests of the lump coal, A, and the fines, B, according to their actual relative weights. By storing only clean lump coal, the danger from spontaneous combustion is minimized, and a better knowledge of the composition is obtained than by any attempt to estimate the proportions of coarse and fines. If such an elaborate system is out of the question, a small proportion of the total load may be dumped separately and shoveled

¹ Bailey and Brady, *J. Ind. and Eng. Chem.* **I**, 161, 263, 316. *Ibid.* **5**, 517.

over an inclined screen, and the parts separately weighed, to obtain a practical estimate.

30. Reduction of Lump Coal for Assay. — The car, or cargo, sample is run through a large jaw crusher to 1.5-inch size, and rapidly reduced by coning and half-shoveling to 50 or 75 pounds. This is now to be reduced to a 2- to 5-pound sample for assay. If the laboratory is near at hand, the whole sample is transferred in iron pails, and, if very moist, is broken to $\frac{1}{2}$ -inch size and dried at a low heat in iron pans (moisture 1). If fairly dry, the sample is broken down at once to pass a sieve of 4 meshes to the linear inch and quartered to 3 or 5 pounds before drying. Samples are preserved in tight fruit jars with screw caps, as already described, if the preliminary reduction must be made at some distance from laboratories. If a sample of 3 to 5 pounds is dried at 15° C. above room temperature, Appalachian bituminous coal and anthracite will be air-dry if placed in the drier in circulating air over night. Illinois coals may require 48 hours and lignites 72 hours for the preliminary air-drying.

31. Reduction to Assay Sample. — Immediately after the last weighing, the entire dried portion should be rapidly pulverized to 10-mesh size; mixed and reduced to 450–500 grams with an inclosed riffle sampler having $\frac{1}{2}$ -inch divisions. If reduction is carried directly to 60-mesh fineness, there will be loss of moisture. With ordinary open grinders, the author finds it most accurate to grind quickly through a 20-mesh sieve, then dry over steam plate, or in an oven below 100° C., for $1\frac{1}{2}$ hours (giving moisture per cent No. 2). 100 grams is afterward reduced to pass a sieve of 60 meshes to the linear inch (25 per cm.).

The Official Committees (35) recommend that the 500-gram sample be ground directly to 60 mesh in a closed porcelain Abbe ball mill at 60 revolutions per minute. Bituminous coals require 1 hour's time and anthracites 2 hours'. The jar should contain about one-third its volume of 1-inch well-rounded pebbles. The best machine for the grinding of 3- to 5-pound samples to 10 or 20 mesh is an inclosed coffee mill or a Hance Bros. & White drug mill with corrugated plates, and fitted with pulleys. In the analysis of the fines another moisture test is often made by drying one hour at 100–110° C. Neither the grinding, or drying, of coals should be carried too far, and uniform conditions must be maintained to obtain satisfactory results. The latest modifica-

tions of standard methods of analysis are found in the reports of coal committees; for which see reference (35) at the close of this chapter.

GOLD AND SILVER BULLION

32. Method of U. S. Mint. — The following description is based on a paper of F. P. Dewey and the practice of refinery chemists, who follow, quite closely, the Mint method. In the purchase of bullion by the Mint the size of the deposit has an important bearing on the sampling. When the weight of a deposit reaches 300 ounces Troy, the samples become important, and with bars weighing 700–1200 ounces, correct work is essential. High-grade bullion and coin gold do not segregate, but when we come to consider bullion of more complex composition, the matter assumes greater importance. It is safe to assume that a “brittle” bar of gold bullion will not be homogeneous. According to Dewey, there is only one satisfactory method of sampling of general gold bullions.

(a) “*Dip*” samples are taken by pouring a small portion of the well-mixed molten metal into water so as to produce globules or granulations. Granulations are sometimes made by pouring directly out of the black-lead crucible into water, the operation of casting being interrupted for the purpose. A good sample of silver bullion is obtained from a silver refining furnace by taking a small “dip sample” directly from the metal bath after every second (1000-ounce) bar cast. The granulations may then be mixed and reduced in size by shears, if necessary, or remelted.

(b) “*Chips*.” — There are various cases where a bar of solid bullion can be satisfactorily tested without melting by cutting a chip with a chisel, preferably of special design. Power-driven punches may be used and machines are also in use which take out a triangular piece of metal by means of a projection on a lever operated by a cam. The chips must be taken from a corner or along the edge of a bar. In systematic sampling of large bars, two chips are generally cut, one from the top and one from the bottom of the bar, and are properly identified.

(c) *Drill samples* are taken according to fixed system, but, in large bars, there is a wide choice in the location of holes. A common practice in the Mint service is to drill halfway through at diagonally opposite corners of the top and unite the drillings for the top sample. The remaining corners are drilled halfway

through from the bottom, and the drillings mixed for the bottom assay. Occasionally, with large bars, the four drillings are kept separate, and sometimes holes are drilled near the center of the bars, also.

Drill samples are often better than chips, especially where large, fairly uniform bars are sampled by a well-designed plan. Drill samples of brittle bars are, however, liable to be inaccurate because of difference between the coarse and fine parts, although on high-grade gold the difference may be as low as .0001 between the top and bottom.

F. P. Dewey concludes that, in sampling bars of gold weighing over 300 ounces, when the assayer is acquainted with the bullion, he may accept either a chip or drill sample. On an unknown bullion, it is unsafe to accept anything but a properly prepared dip sample. Some metal, such as "cyanide" bullion from the cyanide process, must be refined before the gold can be accurately determined.

33. Special Methods of Refineries. — An easy practical way of sampling silver bullion at furnaces, while casting, has been described under the title of "dip samples." Dr. E. Keller, in discussion of the Mint system, suggested that the thin plate method used successfully at anode furnaces for copper, might also be applied to silver bullion.

H. D. Greenwood uses such a method, casting Doré bullion into ($18 \times 7 \times \frac{3}{8}$ inch) plates, which are drilled with $\frac{3}{32}$ -inch holes on the checker-board plan. The drillings are then ground to pass 30 mesh, or a sieve of 12 holes per cm. Any iron is removed from samples with an electro-magnet.

STANDARD METHOD FOR ZINC SPELTER

34. Virgin Spelter, that is, spelter made from ore or raw concentrates by process of reduction and distillation and not produced from reworked metal, is considered in four grades by the American Society for Testing Materials (36), and by the sub-committee on alloys of the American Chemical Society (37). For the methods of analysis and the composition of each grade, refer to methods 31–35, Chapter XIV.

With the exception of two or three minor details, the same procedure is followed by each Committee in the sampling of zinc spelter.

Ten slabs are taken at random from each carload, or lot, received. The first authority permits a smaller sample to be taken for smaller lots, but in no case less than three slabs. In case of dispute, half of the sample is to be taken by the maker and half by the purchaser; and the whole shall then be mixed.

The slabs taken as a sample are to be sawed completely across and the sawdust used as a sample. In case no saw is available, the slabs should be drilled completely through and the drillings cut up into short lengths. The Committee of the American Chemical Society recommend that three 9-mm. holes should be drilled along one diagonal of each slab. One hole should be drilled as nearly as possible at the middle and the others halfway from the middle toward each end of the diagonal line.

No lubricant is permitted in either sawing or drilling. The saw or drill must be thoroughly cleaned, and the sawdust or drilling must be carefully treated with a magnet to remove any particles of iron derived from the tools.

LITERATURE OF SAMPLING

Name	Subject	Reference
1. D. W. Brunton	Mine sampling	Trans. A. I. M. E. 25 , 826. <i>Ibid.</i> 40 , 567.
2. (a) S. A. Reed	Theory of sampling	School of M. Quarterly, 1885.
(b) E. Keller	Pig copper sampling	Trans. A. I. M. E. 27 , 106.
(c) " "	Mattes	Mineral Industry, 10 , 242.
(d) " "	Mathematics of	Eng. and Min. J., 93 , 703.
(e) D. M. Liddell	" "	<i>Ibid.</i> 90 , 897.
(f) A. M. Smoot	" "	<i>Ibid.</i> 93 , 1213.
3. Edmund Kirby	Mine sampling	<i>Ibid.</i> 59 , 196-247.
4. J. A. Church	Machines	<i>Ibid.</i> 86 , 291, 338.
5. T. A. Rickard	Mines	<i>Ibid.</i> 75 , 213-305.
6. Philip Argall	Mines	<i>Ibid.</i> 76 , 888.
7. G. D. Bancroft	Mines	<i>Ibid.</i> 75 , 323.
8. E. E. White	Drill holes	Proc. Lake Sup. Min. Inst. 16 , 100.
9. W. J. Adams	Ore shipments	Mining Sci. Press, 1904, Aug. 6.
10. Wm. Wraith	Molten copper, anodes	Trans. A. I. M. E. 41 , 318.
11. E. Keller	" "	<i>Ibid.</i> 42 , 905.
12. E. A. Hersam	Sizes of Screens	<i>Ibid.</i> 37 , 265.
13. R. H. Richards	Screen standards	Ore Dressing, 3 , 1103.
14. Whitehead & Ulke	Gold bullion	Eng. & Min. J. 66k , 189.
15. F. P. Dewey	Gold bullion at Mints	Trans. A. I. M. E. 43 , 870, 1075.
16. John Jewett	Smelter deductions	Eng. & Min. J. 73 , 217.
17. Bailey & Brady	Accuracy with coal	J. Ind. & Eng. Chem. 1 , 161.
18. G. C. Stone	<i>Sampling Mills</i>	<i>Ibid.</i> 1 , 262.
19. E. P. Mathewson	Anaconda	Eng. & Min. J. 86 , 338.
20.	Greene Cananea	<i>Ibid.</i> 82 , 624.
21. F. F. Colcord	Cobalt, Ont.	<i>Ibid.</i> 82 , 1165.
22.	Garfield, Utah	<i>Ibid.</i> 81 , 509.
23.	U. S. Metals Co.	Mineral Industry, 15 , 300.
24.	Michigan Smelter	<i>Ibid.</i> 14 , 164.
25. Paul Johnson	B. C. Copper Co.	<i>Ibid.</i> 10 , 206.
26. Repath & McGregor	Tooele, Utah	Eng. & Min. J., 90 , 1059.
27.	Copper Queen	<i>Ibid.</i> 82 , 257.
28.	Britannia Co., B. C.	<i>Ibid.</i> 82 , 261.
	<i>Laboratory Machines</i>	
29. Haultain	Design of riffles	Eng. & Min. J. 83 , 232.
30. R. H. Richards	Riffles & samplers	Ore Dressing, 2 , 844, 1570.
31. Snyder	Lab. sampler	Eng. & Min. J. 70 , 549.
32. Calkins	" "	<i>Ibid.</i> 71 , 534.
33. Jones	" riffle sampler	<i>Ibid.</i> 76 , 729.
34. G. A. Disbro	Lab. screens, ratio	Proc. Am. Soc. Test. Materi- als, XIII.
	<i>Sampling of Coal</i>	
35. Committee, E-4,	Report, 1914	Proc. Am. Soc. Test. Mat. XIV, 409.
Joint Committee	Of Amer. Chem. Soc.	J. Ind. & Eng. Chem. 5 , 517.
E. Sommermeier	"Coal Analysis"	
	<i>Zinc Spelter</i>	
36. Committee Report	Specification	Am. Soc. Test. Materials Year Book, 1914, 284.
37. Sub-committee	Approved Report	J. Ind. & Eng. Chem. 7 , 547 (1915).

CHAPTER III

REAGENTS AND STANDARD SOLUTIONS

Introduction. — The following paragraphs treat of the impurities in chemical reagents which may injuriously affect the accuracy of the analysis of copper. The fact that less than .0050 per cent of the usual impurities is required to affect the physical properties of refined copper, together with the demand of consumers for metal of very high purity and of strictly uniform quality, make it necessary to employ for such tests the purest chemicals and to make blank analyses of such reagents. The chemist of the Wallaroo Company has found it necessary to redistil all imported English acids. All acids mentioned in succeeding chapters should be understood to be of the purest commercial grade obtainable and of the maximum strengths given below, unless dilute reagents are locally specified.

Definition of Density. — “Specific Gravity” is a longer term than the one of “Density” lately recommended by the U. S. Bureau of Standards. The author prefers to adopt the latter term for the sake of brevity. *Density* is defined as the weight in grams of a cubic centimeter, or as the *ratio* between the weight of a substance at a fixed temperature (15° or 20° Centigrade) and the weight of an equal volume of water measured at 4° Centigrade, its point of greatest density.

COMMERCIALLY PURE REAGENTS

The formulas for the most important solutions have been arranged in a regular alphabetical order and by number. Such a system is easily added to or interpolated and permits immediate reference to the formula if the numbers are also placed on the corresponding stock bottles.

Hydrochloric acid, HCl (density, 1.18 to 1.20), usually contains a trace of iron and arsenic. The product of the electrolytic process is to be preferred for all arsenic and antimony distillations as it is strictly pure.

Nitric acid, HNO_3 (d., 1.42), should be free from every trace of chlorine and nitrous acid when used for electrolysis or gold assaying. The red-fuming acid for oxidation of sulphides should have a density of 1.60 at least.

Sulphuric acid, H_2SO_4 (d., 1.83–1.84), often contains a trace of arsenic. Some of the high-grade product shows a trace of manganese, which becomes noticeable in the determination of iron and nickel in refined copper.

Ammonium Hydroxide, NH_4OH (d., .90), unless of extreme purity, will show injurious amounts of iron in addition to the usual traces of pyridine. Not more than .0001 per cent of the latter should be present in ammonia used for the separation of arsenic or antimony from copper by precipitation with excess of ferric salts.

PREPARATION OF PURE GASES—CARBON MONOXIDE

Carbon Monoxide, CO , may be prepared by dropping strong sulphuric acid into 98 per cent formic acid.¹ The acid is placed in a small flask, and the gas must be purified from a little carbon dioxide by passing it through potassium hydroxide solution, then through alkaline pyrogallate of potassium to remove traces of oxygen, and finally through drying tubes.

To secure an even flow of gas, raise the temperature of the flask.

CARBON DIOXIDE

Carbon dioxide, CO_2 , may be obtained in a very pure state by dropping strong sulphuric acid into a flask half filled with a thick paste of sodium bicarbonate and water, as recommended by Bradley and Hale.²

This method is inconvenient for analytical purposes. Gas of sufficient purity for use in the "Determination of oxygen in copper" (Chapter XIII) is generated by the action of dilute hydrochloric acid on lumps of white marble. The traces of oxygen present are absorbed by passing the gas through a 15-cm. roll of red-hot copper gauze, contained in a 25-cm. ignition tube. To avoid rapid deterioration of the copper, the burner should not be lighted until the air has all been driven out of the bottle and tubes. The coil is easily regenerated by reversing the valves, opening a stopper in the rear of the tube, and passing hydrogen

¹ E. Rupp, *Chem. Ztg.* **32**, 983.

² J. Am. Chem. Soc. **30**, 1090.

gas from a second generator for 15 minutes. The purification train of tubes may be arranged in order thus: (a) Casamajor generator, or a small Kipp with pressure tube above; (b) Bulb of saturated neutral potassium permanganate, or mercuric chloride, for absorption of hydrocarbons; (c) U-tube of silver sulphate; (d) Bowen's potash bulb with strong sulphuric acid; (e) Tube with the roll of copper gauze; (f) Two drying tubes of calcium chloride, sulphuric acid, or phosphorous pentoxide, as preferred.

HYDROGEN

Hydrogen gas may be more easily purified if it is generated by pure zinc and dilute sulphuric acid (not hydrochloric acid). A. M. Smoot recommends the addition of one drop of platinic chloride solution to two liters of (1:4) acid. The purifying train consists of: (a) The generator, or gas cylinder; (b) Allihn washing bottle of 10 per cent potassium hydroxide, saturated with potassium permanganate; (c) Tubes for the removal of traces of oxygen. Here there is a choice of at least three alternatives, the first being preferred, — (1) Allihn 250 c.c. bottle of potassium hydroxide solution (d., 1.27) in which is dissolved 5 grams of pyrogalllic acid; (2) a heated tube of 5 per cent palladium asbestos; (3) a tube containing a long roll of reduced copper gauze heated by a short furnace; (d) Finally, two tubes of drying agents, as described under "Oxygen," Chapter XIII.

SULPHUR DIOXIDE

Sulphur dioxide, SO_2 , has been obtained by heating turnings of copper with sulphuric acid. Whenever a cylinder of the compressed gas is not at hand, the easiest method of generation consists in dropping a saturated solution of sodium sulphite from a separatory funnel, through a tube of soft glass, which dips under the surface of 400 to 500 c.c. of sulphuric acid, contained in a liter flask.

NOTE. — *Oxygen*, O_2 , simply requires a purification from traces of carbon dioxide, with the addition of drying tubes, unless it is to be used for the combustion of carbon. In that case, a heated catalyzer tube should precede the potassium hydroxide.

STANDARD SOLUTIONS

The standard solutions are numbered as a means of ready reference, and are those employed in the methods described in succeeding chapters.

Unless otherwise specified, they are made with the commercially pure reagents, sold as "chemically pure."

1. Acid Mixture, for the electrolytic assay of copper (method 2, Chapter XI). This mixture, which has been adopted by several works, permits direct electrolysis without any evaporation, as soon as the copper drillings are dissolved upon the steam plate and the solution diluted. It is made up in large quantities in the following proportions *by volume*: 7 parts of nitric acid (d., 1.42), 10 parts of sulphuric acid (d., 1.84), and 25 parts of distilled water, strictly free from chlorides.

2. Ammonium Oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. — A saturated solution is used for the precipitation of calcium, or, if preferred, a 10 per cent solution of the crystals. 10 c.c. of the latter precipitates about .4 gram CaO .

3. Ammonium Molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, is required in the titration of lead in the "Western method" for ores or slags (Chapter V). Dissolve 4.3 grams in 200 c.c. of water, add a few drops of ammonia, and make up to one liter. 1 c.c. is nearly equivalent to .005 gram of lead (Pb). To standardize, dissolve .200 gram of chemically pure lead foil in dilute nitric acid. Make the liquid alkaline with ammonia, boil for a minute, then render the solution acid with acetic acid and titrate. Use a solution of 1 gram of tannin in 300 c.c. of water as an indicator. Deduct the amount of molybdate required to affect the indicator from the total amount discharged from the burette.

4. Ammonium Molybdate is also employed as an indicator in the titration of zinc. Prepare a 1 per cent solution with distilled water.

5. Ammonium Acetate, $(\text{NH}_4\text{C}_2\text{H}_3\text{O}_2)$, is used as a saturated solution in the extraction of lead from various precipitates, such as silica, or barium sulphate (Chapter V). Glacial acetic acid may be very slowly added to concentrated ammonium hydroxide until the liquid is slightly acid. For ordinary work, the solution may then be made slightly alkaline.

6. Ammonium Phosphate, Secondary, $(\text{NH}_4)_2\text{HPO}_4$, may be

made up as a 10 per cent solution for the precipitation of magnesium. 1 c.c. will precipitate about .0305 gram of the oxide, MgO. The same reagent is employed in the "Phosphate method" for alumina, described in Chapter V.

7. Ammonium Sulphydrate, NH_4HS , must be frequently prepared, as it does not keep unaltered many days. Saturate strong ammonia, free from pyridine, with pure hydrogen sulphide until the iron is precipitated as black sulphide and the supernatant liquid is yellow. After settling, the solution should be filtered into a brown glass-stoppered bottle.

8. Ammonium Thiocyanate, NH_4SCN , is required as a precipitant, and also as a standard volumetric solution. In method 3, Chapter IV, a solution of 40 grams per liter is adopted as a precipitant of copper in the assay of copper in ores.

9. Ammonium Thiocyanate for the titration of silver arsenate, in method 12, Chapter V, is made of such a strength that 1 c.c. equals .001 or .005 gram of arsenic. It is standardized against a weighed quantity of pure silver dissolved in nitric acid. 107.88 parts of silver = 25 parts of arsenic.

10. For method 7, Chapter IX, the *thiocyanate*, or sulphyocyanate, is adopted as a finishing solution in the refinery method for titration of silver bullion, following a standard solution of hydrochloric acid (19). 1 c.c. equals .001 gram of metallic silver.

11. Ammonium Thiocyanate, as a precipitant of copper in complete analysis of the metal, is prepared by dissolving 1 pound, or 453.6 grams, of the crystals in 2 liters of distilled water. 1 c.c. will precipitate about 0.12 gram of copper in the presence of an excess of sulphur dioxide, sufficient to saturate the solution and complete the reduction of the precipitate to the white cuprous thiocyanate.

12. Barium Hydroxide, $\text{Ba}(\text{OH})_2$, is employed in the form of a saturated solution for the absorption of carbon dioxide in steel analysis, or for carbon, etc., in ores. Stir 20 grams of the hydroxide in 1 liter of hot, freshly boiled distilled water, and after settling, filter quickly through a covered funnel into a closed flask, provided with a rubber stopper perforated for two tubes. Through one hole is passed the stem of a 100 c.c. pipette, and through the other, a short bent tube of soda lime to protect the liquid from the carbon dioxide of the air. For each analysis, 90 to 100 c.c. are pipetted into a straight 10-bulb absorption tube.

13. Barium Chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. — A solution of nearly 10 per cent strength is used as a precipitant only.

14. Bismuth Sulphate. — For the color method of F. B. Stone, in the analysis of refined copper (7, Chapter XIII). Dissolve the chemically pure metal, or oxide, evaporate with a slight excess of sulphuric acid until any other acid is removed, then dilute until 1 c.c. contains .0001 gram of bismuth. In making color tests, a little sodium sulphite solution is added to decolorize any trace of ferric salt.

15. Cadmium Chloride, CdCl_2 , in an ammoniacal solution, absorbs sulphur, when evolved as hydrogen sulphide from metals. Dissolve 12.5 grams of the chloride (according to J. M. Camp), in 125 c.c. of water, add 100. c.c. of ammonia (d., .90), and filter. Then dilute to 1 liter.

10 c.c. are taken for the absorption of the sulphur from 5 grams of steel, and about 5 c.c. for sulphur evolved during the reduction of copper by hydrogen (method 15, Chapter XIII).

16. Copper-Potassium Chloride is used as a solvent of steel, which permits the separation of carbon. It is prepared by dissolving 1 pound, or 453.6 grams, of the green crystals in 1 liter of distilled water, filtering through a plug of ignited asbestos, and adding 50 c.c. of strong hydrochloric acid. For carbon in nickel alloys, a saturated neutral solution is adopted, adding acid to each analysis (16, Chapter XIV). The tops of the bottles should be protected from dust.

17. Cupric Chloride, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, as a solution of 300 grams of crystals in 1 liter of hydrochloric acid (d., 1.20), is combined with No. 58 to make a distilling solution for arsenic (method 10, Chapter V).

18. Ferric Ammonium Sulphate, $\text{Fe}_2(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 12 \text{H}_2\text{O}$, as a 10 per cent solution, is added to copper solutions as a precipitant of the arsenic group of metals. *Ferrous ammonium sulphate* is much used to standardize permanganate, but the results do not always agree with metallic iron. A special solution, No. 40, is used with No. 39 for manganese.

19. Hydrochloric Acid, HCl , diluted to the "normal" solution (36.468 grams of HCl per liter) is run against soda in alkalimetry. For method 7, Chapter IX, a solution is prepared of such a strength that 100 c.c. precipitates a few milligrams less than 2000 milligrams of silver.

20. Standard Iodine. As a titrating solution for arsenic in ores (Chapter V), dissolve 12.828 grams of pure iodine and 19 grams of potassium iodide in 200 c.c. of water and dilute to 1 liter. 1 c.c. nearly equals .005 gram of arsenious oxide, As_2O_3 . To standardize, dissolve .2 gram of pure arsenious oxide in a very little sodium hydroxide.

Dilute to 300 c.c., make acid with sulphuric acid, using only one or two drops of dilute acid in excess, as determined by a floating piece of litmus paper. Add an excess (4 to 10 grams) of sodium bicarbonate, then 3 c.c. of No. 56 starch solution, and titrate cold to a purplish blue.

21. Iodine Solution, for the titration of arsenic from refined copper, is made by dissolving 3.5 grams of "reagent" iodine with 7 grams of the potassium iodide in a little water and diluting to 1 liter. Allow to stand a day before use. 1 c.c. titrates about .001 gram of arsenic, and about .04 c.c. is required to produce the end-point. Standardize with .06 gram of the purest (99.9 per cent) arsenious oxide, just as for solution 20, but add five drops of a 10 per cent solution of potassium iodide to the arsenious solution immediately after the starch. The iodide is added to obtain a definite end-point and an immediate formation of iodide of starch in presence of very small amounts of arsenic. See method 6d, Chapter XII.

22. Iodine Solution for the titration of hydrogen sulphide (when liberated from cadmium sulphide in the determination of sulphur in steel, or of oxygen in copper), may be made of such strength that 1 c.c. equals .0025 gram of sulphur. To obtain this strength, dissolve 2 grams of purest "reagent" iodine in 100 c.c. of water with 5 grams of potassium iodide and dilute to 1 liter. For very exact work, the iodine solution may be made by Payne's formula. — See "Methods of Iron Analysis," by F. C. Phillips, page 22.

23. Magnesium Sulphate, $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$, is used in the form of the well-known "magnesia mixture" for the precipitation of *arsenic* and phosphoric acids. Magnesium sulphate is better than the chloride because it contains only one-fifth as much calcium salt, which is present as an impurity. Fresenius' formula gives good results: — Dissolve 1 part of magnesium sulphate crystals, 4 parts of ammonium chloride, and 4 parts by volume of ammonia water (d., 0.9) in 8 parts of water. Allow impurities to

settle and then filter. An old solution, which has perceptibly attacked the glass, should be rejected unless any precipitated silica is deducted.

24. Magnesium Chloride, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, for the separation of phosphoric acid from ores, slags, or limestone (Chapter V), may be made up by the formula of A. A. Blair. Dissolve 110 grams of the crystals in water and filter. Dissolve 280 grams of ammonium chloride in water, add a little bromine water, and a slight excess of ammonium hydroxide, heat nearly to boiling, and then filter. Mix the two liquids, render the mixed liquid faintly alkaline, dilute to 2 liters, shake occasionally, allow to stand two or three days, and filter a portion into a small bottle as required. 10 c.c. precipitates .15 gram of magnesium oxide, MgO .

25. Manganous Sulphate, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, is combined with phosphoric acid to make a titrating solution known as the Zimmerman-Reinhardt mixture. It is added in their method for the titration of reduced iron by potassium permanganate, in order to obtain a clear end-point. Dissolve 160 grams of the manganese salt and dilute to 1750 c.c. Add 330 c.c. of strong phosphoric acid and 320 c.c. of concentrated sulphuric acid. 10 to 20 c.c. of the mixture are added to each iron solution after reduction of the iron by stannous chloride and mercuric chloride. The preceding is the improved formula of Mixer and Dubois.

26. Mercuric Chloride, HgCl_2 , is used as a saturated solution. 5 c.c. are added to a solution of ferrous iron after reduction by stannous chloride, in order to destroy the slight excess of the latter, which should not be more than one or two drops.

27. Mercuric Nitrate is used for the amalgamation of copper borings in the "assay of gold in copper" (method 3, Chapter X). Twenty-five grams are dissolved in one liter. A saturated solution of the sulphate in dilute sulphuric acid is even better. Take 10 c.c. of the nitrate, or 25 c.c. of the sulphate for each "assay ton" sample of copper.

28. Dimethyl Glyoxime, for the precipitation of nickel in ammoniacal solution, is dissolved in the proportion of 1 gram to 100 c.c. of ethyl alcohol. — Used in method 3, Chapter XIII.

29. Nitroso- β -Naphthol is employed as a precipitant for cobalt and for the separation of cobalt from nickel (method 2, Chapter XIII).

Dissolve the salt in acetic acid of 50 per cent strength until the acid is saturated.

30. Potassium Cyanide, KCN, for the titration of copper in ores and mattes, according to "western methods." Dissolve 22.5 grams in water and make up to one liter. Use the chemically pure salt. 1 c.c. equals .005 gram of copper. Standardize it with matte, or ore, in which the copper has been determined electrolytically.

31. Potassium Cyanide, for the titration of nickel in ores, or mattes, is made of a strength of 24.5 grams per liter and standardized against pure nickel, and diluted so that 1 c.c. equals .005 gram nickel (method 1, Chapter VII).

32. Potassium Ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$. — For a standard solution, to be used in the titration of zinc in ores and slags, dissolve 21.63 grams of the salt with 7 grams of sodium sulphite crystals in water and make up to 1 liter. 1 c.c. is equivalent to nearly .005 gram of zinc. To standardize, dissolve .200 gram of chemically pure zinc, or freshly ignited chemically pure zinc oxide, in 15 c.c. of hydrochloric acid. Add 7 grams of ammonium chloride. Dilute to 200 c.c. with boiling water and titrate, using a solution of one gram of ammonium molybdate in 100 c.c. of water for an indicator. Deduct amount of ferrocyanide required to affect the indicator from the total amount used (methods 16 and 17, Chapter VII).

33. Potassium Ferrocyanide, as a standard solution for the titration of zinc in brass and German silver (Chapter XIV), is prepared as follows: Dissolve 80 grams of the salt in 2500 c.c. of distilled water, and allow to stand at least six weeks before use, to obtain a permanent solution. To standardize, weigh 2 grams of zinc, dissolve in nitric acid, and make up to one liter. Take 100 c.c. (.2 gram) zinc, add 5 c.c. nitric acid, 3 c.c. strong ferric chloride solution, 20 c.c. of saturated citric acid solution, dilute, and make distinctly alkaline with ammonia. The final volume should be 250 c.c. Boil the liquid and titrate the boiling solution. Fill pits in a porcelain test plate with 50 per cent acetic acid, and add 2 drops of zinc solution to determine the end-point which changes from greenish to clear blue. The correction for the amount necessary to reach the end-point in a solution free from zinc, must be made by each operator, and is about $\frac{1}{2}$ c.c.

34. Potassium Bichromate, $K_2Cr_2O_7$, is used to make up a standard titrating solution for iron in the "Western methods" for ores (Chapter V).

Dissolve 3.408 grams in water and make up to one liter. 1 c.c. is equal to approximately .005 gram of ferrous oxide, FeO . With 4.39 grams of fused salt per liter, the iron value is about .005 gram per c.c. To standardize in terms of iron, or ferrous oxide, dissolve .2 gram of analyzed iron wire in 10 c.c. of (1:1) hydrochloric acid with the addition of a few crystals of potassium chlorate to destroy any trace of organic matter. Or 1 gram of pure ferrous ammonium sulphate may be dissolved in 100 c.c. of hot water and 10 c.c. of the hydrochloric acid. In either case, add one or two drops of stannous chloride in excess of the amount required to decolorize the liquid.

Remove this excess of stannous chloride by adding 5 c.c. of a saturated solution of mercuric chloride, which should produce a white (not dark) precipitate. Cool by diluting to 300 c.c. or more and titrate. Test drops of the liquid on a porcelain tile with a drop of potassium ferricyanide.

35. Potassium Hydroxide, KOH . — A normal solution is 56.1 grams per liter. Potash (purified by alcohol) should not be used for gas analysis.

36. Potassium Chromate, as adopted in the Guess method for lead in ores, or mattes, is made up with 100 grams of the salt, K_2CrO_4 , per liter. 1 c.c. precipitates about 106 milligrams of lead.

37. Potassium Iodide, KI , in the form of a 10 per cent solution, is added in the titration of arsenious oxide by standard iodine (No. 20) in order to have the ions required to produce an immediate formation of the iodide of starch with the slightest excess of iodine, even when the solution titrated contains but a trace of arsenic. Add five or six drops after the solution has been made alkaline by the large excess of sodium bicarbonate. The titration is described in detail under the "Determination of arsenic in refined copper" (method 6d, Chapter XII).

38. Potassium Iodide, KI , is also employed as an active reagent for the titration of nickel in matte (method 14, Chapter VI). 40 grams are dissolved in 1 liter.

39. Potassium Permanganate, $KMnO_4$, for the titration of moderate amounts of iron in solution, is made up of such a

strength that 1 c.c. will oxidize about .005 gram of iron. To this end, dissolve 2.86 grams in water and dilute to 1 liter. This strength may be doubled for iron ores or any rich material. The iron (Fe) value of 1 c.c. multiplied by .2951 gives the value in terms of manganese (Mn.), as determined by Volhard's method. The solution is standardized by various methods in different laboratories. The author prefers soft iron wire of known composition, for the determination of the iron value. In the titration of small amounts of manganese in copper ores, the value in terms of manganese may be found by multiplying the value in calcium oxide, CaO, by .5878.

40. Potassium Permanganate, for the titration of oxalate of calcium, obtained from copper ores and slags, may be best standardized by perfectly dry, pure sodium oxalate. The strength of permanganate employed in "western methods" is 5.643 grams per liter. 1 c.c. is nearly equal to .005 gram calcium oxide, CaO. 56.07 parts of calcium oxide, CaO, require 134 parts of very pure standard oxalate. The salt should be thoroughly dried in an air oven at 100° C. and preserved in a small glass-stoppered bottle. Sodium oxalate \times .41843 equals CaO, and 1 part of iron (Fe) equals .50206 part of calcium oxide (CaO).

41. Potassium Permanganate, for the estimation of manganese by the "bismuthate method," is made up very dilute and run against a special ferrous-ammonium-sulphate solution (42) or with sodium arsenite (47). A .03 normal solution (1 gram per liter) will titrate conveniently .02 gram of manganese (Mn). For rich ores, use a .1 normal solution (or 3.1 grams per liter).

42. Special Ferrous Ammonium Sulphate, for the "bismuthate method," is dissolved to form a solution of 12.4 grams of the salt.

The concentrated liquid is then treated with 50 c.c. of a mixture of equal volumes of strong sulphuric acid and strong phosphoric acid, and diluted to exactly 1 liter. This will give a standard solution almost equal to the weaker .03 normal permanganate (41). For .1 normal permanganate, use 39.2 grams of the iron salt and double the amount of the two acids employed. See volumetric method for chromium (15, Chapter VI).

43. Potassium Thiocyanate, KSCN, is dissolved and diluted to such a degree that 1 c.c. will precipitate about .12 gram of

copper. Refer to solutions 7 and 8, and method 1, Chapter XII. For ores, a more dilute solution of 40 grams of the crystals per liter is sufficient, as described in method 3, Chapter IV.

44. Silver Nitrate, AgNO_3 , is employed in method 5, Chapter V, as a precipitant of arsenic acid. Make a 10 per cent solution by weight and use 7 c.c. for .1 gram of arsenic.

45. Silver Nitrate, in method 1, Chapter VII, is used as an indicator in the titration of nickel. One gram is dissolved in water, and the solution brought to a volume of 1 liter.

46. Silver Nitrate, for the precipitation of chlorine in copper electrolyte, is made up as a normal solution of 169.89 grams per liter. 1 c.c. will combine with .03546 gram of chlorine. For very exact standardization, the solution would, of course, be run against standard salt solution, or standardized ammonium thiocyanate (No. 9).

47. Sodium Arsenite. — A stock solution is made by heating in a flask on a water bath 15 grams of arsenious oxide (As_2O_3), 45 g. of sodium carbonate and 150 c.c. of water. Cool and make up to 1000 c.c. with water. A standard solution of the proper strength for titration of chromium or manganese in ores or metals is made by diluting 300 c.c. to 1 liter and standardizing it with permanganate. The value of the permanganate itself is best obtained by comparison with pure sodium oxalate (see 25, chapter VI).

47 a. Sodium Citrate, — 200 grams per liter, is a reagent for 1, Chapter VII.

48. Sodium Chloride, NaCl , in the assay of copper bullion, Chapter X, is a precipitant of silver. If 19 grams are dissolved in 1 liter, 1 c.c. will precipitate 350 milligrams of silver. Refer also to No. 17.

49. Sodium Hydroxide, NaOH , is made up as a normal solution for the determination of the free acid in copper electrolyte, as described in Chapter IX. Dissolve 40 grams of the purified sticks in 1 liter, and standardize against normal sulphuric acid, using a .1 per cent aqueous solution of methyl orange as an indicator. The acid is valued by titrating it against .8-gram portions of chemically pure sodium carbonate, which has been ignited just below a red heat.

50. Sodium Thiosulphate (or hyposulphite), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, is the titrating solution in the "iodide method" for copper in

ores or mattes, as given in method 2, Chapter IV, also in method 22, Chapter VI. If 19.59 grams are dissolved in 1 liter, 1 c.c. will react with about .005 gram of copper.

51. Sodium Phosphate, secondary, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, is dissolved to form a 10 per cent solution of the crystals, for the precipitation of either aluminum, magnesium, manganese, or zinc. The ammonium salt (5), when it is permissible, is preferable to the sodium compound, as the ammonium salt is easily volatilized, if traces are inclosed in a washed precipitate.

52. Sodium Sulphide, Na_2S , as a filtered solution of the pure commercial salt, extracts or separates the sulphides of the "arsenic group" of metals from copper, lead, or silver, but not so well from bismuth, unless a little potassium hydroxide is added.

A filtered solution with a density of 1.08 is diluted with about two parts of water for use in copper analysis. For electrolysis of antimony sulphide, it is necessary to provide a strictly colorless monosulphide. The yellow color may be removed by heating with sodium peroxide, hydrogen peroxide, etc., or the sodium sulphide may be prepared by a method described by A. Classen and H. Koch. Dissolve about 60 grams of the purest commercial sodium hydroxide in water, dilute until the liquid has a density of about 1.2, then saturate one half of the liquid with hydrogen sulphide. Add the other half of the solution, and if the monosulphide is required, filter the solution directly into stoppered bottles. Dilute for use, according to conditions.

53. Stannous Chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, for reduction of iron. Dissolve metallic tin foil in hydrochloric acid, or use the formula of J. M. Camp:—Dissolve 300 grams of chloride crystals in 500 c.c. of strong hydrochloric acid and 500 c.c. of water. Boil with a few scraps of tin until clear and then bottle. 1 c.c. reduces about 1 gram of iron.

54. Normal Sulphuric Acid, H_2SO_4 , is produced by mixing with water an amount of the acid equivalent to 49.04 grams of the 100 per cent acid, and then diluting to 1 liter. It is standardized against sodium carbonate ignited, and may be compared with normal sodium, or potassium hydroxides (Nos. 35 and 49). Use an aqueous solution of methyl orange as an indicator, except in cases where bicarbonates are to be estimated.

In very accurate work, the temperature should be noted with each titration, to apply a correction, if necessary.

55. Standard Titanium Solution, for method 13, Chapter VII, is prepared by dissolving the pure oxide by fusing it, or by treating with 10 c.c. of hot strong sulphuric acid and 5 grams of potassium bisulphate. The solution is mixed with dilute sulphuric acid at first, to prevent precipitation. Then add water until 1 c.c. contains 1 milligram of titanic oxide, TiO_2 .

56. Starch Indicator (for titrations with iodine). — According to the formula of J. M. Camp, add to .5 gallon (2 liters) of boiling water about 25 grams of pure wheat starch, previously stirred up into a thin paste with cold water. This is boiled for ten minutes, and, when cold, about 25 grams of pure zinc chloride dissolved in water are added and the solution diluted to 1 gallon, or 3800 c.c. Mix thoroughly and allow to settle over night; siphon the clear solution into a glass-stoppered bottle. It will keep indefinitely. This preparation is suitable for the titration of the acidified solution of cadmium sulphide obtained in the evolution method for sulphur in steel.

57. Special Starch is prepared by hydrolyzing the ground material with 1 per cent hydrochloric acid, allowing it to stand over night in the cold; then filtering, and washing with cold water.

Dry the washed starch and heat for three hours in the air oven at 100°C . Dissolve 2 grams of this starch in 500 c.c. of boiling water, and add 15 drops of oil of cassia to prevent fermentation (method 6, Chapter XII).

58. Zinc Chloride, ZnCl_2 , finds its principal use in a copper laboratory as one ingredient of a concentrated distilling solution used by chemists in the western states for the distillation of arsenious chloride from the sulphide in the analysis of ores.

Distilling Solution. — Dissolve one pound (453.6 grams) of chemically pure zinc by adding to it gradually a mixture of 1250 c.c. of hydrochloric acid (d., 1.2) and 500 c.c. of water. When the zinc has dissolved, evaporate the solution to 1100 c.c. and mix the whole amount with 1 liter of the concentrated solution of cupric chloride (No. 17).

CHAPTER IV

THE ASSAY OF COPPER IN ORES AND FURNACE PRODUCTS

THIS chapter is restricted to the assay of copper in its solutions. The following methods are in regular use for the estimation of copper in ores, native copper, furnace by-products, or mill tailings: — (1) titration with potassium iodide;¹ (2) titration with potassium cyanide;² (3) precipitation with potassium thio-cyanate and titration of the resulting compound with potassium permanganate in presence of excess of caustic alkali;³ (4) the colorimetric assay;⁴ (5–9) electro-analysis.⁵

The selection of method varies with the character of the material and the preference of the chemist, but the electrolytic assay is the most accurate.

1. Titration by Iodide.¹ — According to standard western practice, the weighed sample of 1 gram (.5 for ores over 25 per cent copper), is decomposed in a 3-inch (7.5 cm.) casserole by treatment with nitric and hydrochloric acid in excess and 10 c.c. of sulphuric acid.

Evaporate until dense white fumes of the last acid are evolved. After cooling, dilute with water and boil until all soluble sulphates are in solution. Filter off the insoluble residue and wash well with hot water, allowing the filtrate and washings to run into a 350 c.c. beaker. To this filtrate add 10 c.c. of a saturated solution of sodium thiosulphate and boil until the precipitated sulphides settle readily. Filter and wash with cold water until free from iron salts (usually 4 to 7 times). Carefully wrap the paper, fold it into a dry filter, and place it in a porcelain crucible. The crucibles are placed in a muffle that is kept

¹ Method 1. *Eng. and Min. Jour.* **89**, 498; *J. Am. Chem. Soc.* **24** (1902), 1082 and 580; *Eng. and Min. Jour.* Nov. 17, 1904; (1910) 1221; **74** (1902), 846.

² *Low's Technical Analysis.* ³ *J. Am. Chem. Soc.* **20** (1898), 610.

⁴ *J. Am. Chem. Soc.* **19** (1897), 24; *Trans. A. I. M. E.* **30**, 851.

⁵ *Eng. and Min. Jour.* **84**, 773; also **77** (1909), 159; **94**, 315. *J. Am. Chem. Soc.* Nov. 1907. *El. Chem. and Met. Ind.* **6**, 19 and 58.

barely red hot, to roast and dry the precipitate, thus removing the sulphur and much of the arsenic. Too much heat must be carefully avoided at this stage, or the mass will spit before it is dry, and later on will fuse into the porcelain. It is to prevent "spitting" that the extra filter paper is used, and when properly ignited, the residue will be found enveloped in ash, and easily transferable to a flask.

Now transfer the residue to a small "copper flask," decompose it with 5 c.c. of nitric acid-potassium chlorate mixture, and evaporate almost to dryness to oxidize any remaining arsenic, etc. Add dilute ammonia to alkaline reaction and boil the liquid well for two minutes. Acidify slightly with acetic acid without boiling, cool, and add about 3 grams of solid potassium iodide. Determine the copper by titration with sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), using starch as an indicator. (Solutions 48 and 54, Chapter III.)

The Western chemists, just quoted, did not find the reduction of copper by aluminum to be satisfactory. It not only took more time, but with special ores and conditions, the precipitation was not complete. Besides, particles of the fine copper were easily lost on filtering, or were oxidized and dissolved by the wash water.

Reduction by Aluminum. — A. M. Fairlie,¹ A. H. Low,² and others prevent oxidation of the copper by the addition of 15 c.c. of hydrogen sulphide water as soon as the reduction by aluminum is completed. This scheme prevents the formation of a bulky mass of sulphides from rich ores. If such reduction is preferred, it may be effected after all silver chloride has been filtered off, by boiling the sulphuric solution in a wide lipless beaker with three pieces of sheet aluminum, each $1\frac{1}{2}$ inches (or 3.8 cm.) square. Continue the boiling until the copper is out of solution and the aluminum appears bright and clean on shaking. Pour through a 9 cm. filter directly after the addition of the hydrogen sulphide water, but hold back most of the metal and wash it two or three times with diluted hydrogen sulphide water. Drain thoroughly and redissolve through the funnel by 10 c.c. of dilute (1:1) nitric acid. Finally, wash the aluminum

¹ *Eng. and Min. Jour.* **84**, 773; also **77** (1909), 159; **94**, 315. *J. Am. Chem. Soc.* Nov. 1907. *El. Chem. and Met. Ind.* **6**, 19 and 58.

² *J. Am. Chem. Soc.* **30** (1908), 760.

well, cleanse any sulphur on the filter by treatment with 5 c.c. of saturated bromine water, and finish the washing with hot water. Boil out all the bromine and titrate by iodine as before.

Kendall¹ recommends the addition of sodium hypochlorite and phenol in order to secure more even results in the titration, and A. H. Low² advises a slight boiling after the addition of the acetic acid to prevent a return of color after titration. Refer also to the special "iodide" titration of nickel in nickeliferous copper matte (14, Chapter VI).

2. Titration with Potassium Cyanide.²—The action of this reagent on copper solution is a function of several variables. The conditions observed in standardization must be exactly observed in the work on the ore samples. The main points are uniform temperature, regularity in titration, the same excess of alkali, and the same final volume, in each case.

Standard Solution.—22.5 grams of chemically pure potassium cyanide per liter make a solution, 1 c.c. of which will have a value of about .005 gram of copper. Refer to formula 28 of Chapter III.

Unless the ores are very impure, western operators usually prefer to standardize against matte, or ores, in which the copper contents have been determined electrolytically. Others prefer, instead, to take .2 gram to .3 gram of chemically pure copper foil, dissolve in 5 c.c. of strong nitric acid, dilute with 5 c.c. of saturated bromine water plus 25 c.c. of distilled water, and boil out the bromine. Add 10 c.c. of ammonia (d., .90) with 50 c.c. of water and cool quickly to room temperature, then titrate exactly as for ores.

The standard cyanide is subject to change, and it is necessary to protect the liquid from the sun, or any strong light, and retest it frequently.

(a) *Assay of Pure Ores.*—Such ores, or standard mattes, are dissolved in nitric acid. Add 10 c.c. of strong acid to 1 gram of sample in a 500 c.c. flask. Take only .5 gram when over 25 per cent copper. Heat on a steam bath until the brown fumes are driven off, then add 200 c.c. of cold water and 20 c.c. of ammonium hydroxide (d., .90). Titrate slowly, adding potassium cyanide in small amounts only and allowing the deposit

¹ *J. Am. Chem. Soc.*, **33** (1911), 1947; **34**, 347.

² Personal communications.

to settle after each addition. When the solution in the flask is a pale violet color, filter into another 500 c.c. flask and add the cyanide until colorless. The burette reading is multiplied by the factor for its copper value, which is determined by running a half-gram sample of "standard" matte as a standard with each set of assays.

(b) Samples containing organic matter, or much arsenic or manganese, are decomposed with nitric acid and a small amount of potassium chlorate. Large amounts of organic matter may keep some iron in solution, producing greenish tints. In this case, roast sample gently in a scorifier; then treat the residue in a platinum dish with 5 c.c. of nitric acid, 5 c.c. hydrofluoric acid, and 2 c.c. sulphuric acid, and evaporate to fumes of sulphuric anhydride. Add 5 to 10 c.c. of nitric acid, wash into the flask, and proceed as before. Good results are often obtained by adding small portions of potassium chlorate to the boiling nitric acid solution. Some oxidized ores and slags require a preliminary treatment with hydrochloric acid or the addition of hydrofluoric acid for complete solution of the copper. In such a case, add 5 c.c. of each of the acids, heat gently for ten minutes, add 10 c.c. of nitric acid, and take to dryness. Take up with water and 5 to 10 c.c. of nitric acid, wash into the flask, and proceed as before. If much silver is present, remove it with a few drops of hydrochloric acid before adding the ammonia to any of the samples under treatment.

(c) *Impure Ores, or Mattes, etc.* — In presence of much zinc, cobalt, or nickel, a preliminary separation of the copper must be made, preferably by sodium thiosulphate, as in method 1. The roasted sulphides should be dissolved in nitric acid and titrated as before, except that chemically pure copper foil is used for the standard, because the titration is made in the absence of iron.

3. Thiocyanate Method (By F. G. Hawley).¹ — Weigh .5 to 1 gram of ore into a tall 300 c.c. beaker, add 12.5 c.c. of "acid mixture" (1 part sulphuric acid, 2 parts nitric acid and 1 of a saturated solution of potassium chlorate in nitric acid). Then, when nearly decomposed, add 10 drops of hydrofluoric acid, evaporate to strong white fumes of sulphuric acid, and cool the residue. Add 60 c.c. of water and just neutralize with ammonia. Add 5 c.c. of hydrochloric acid, then 10 to 12 c.c. (according to cop-

¹ *Eng. and Min. Jour.* **90** (1910), 647.

per content) of potassium thiocyanate (40 grams per liter). Boil for two minutes and remove from the plate. Let the beaker stand for 5 minutes covered, then for 5 minutes uncovered, and filter through a 12.5 cm. filter, No. 597 S. and S. Wash four times with hot water (60 to 70°), then place the original beaker under the funnel, and, with a wash bottle, treat the copper salt with a boiling 5 per cent solution of sodium hydroxide. Use a medium fine jet and stir the precipitate thoroughly. Wash four times with hot water, cool the filtrate somewhat, make acid with slightly diluted sulphuric acid, and immediately titrate with standard potassium permanganate, — of which 1 c.c. equals .01 gram of metallic iron, Fe. High coppers should be titrated cold and in a volume of not less than 200 c.c. A conversion table is employed. The thiocyanate may also be dissolved as in **5c** and the solution electrolyzed.

3a. Method of D. J. Demorest.¹ — This modification is said to permit an accurate titration by permanganate without the use of any empirical conversion table. Weigh out enough of the ore to have present .05 to .30 gram of copper. Transfer the sample to a 200 c.c. beaker, add 5 c.c. of strong hydrochloric acid, and heat for several minutes; then add 10 c.c. of nitric acid and digest on a hot plate until the ore is completely decomposed. Then add 10 c.c. of (1:1) sulphuric acid and boil down until white fumes appear. Cool, add 50 c.c. of water containing 3 grams of tartaric acid, and heat until all soluble salts are in solution.

Cool and add ammonia until the solution turns a deep blue, then add sulphuric acid until the liquid is just acid, then 1 c.c. more. Now add 1 gram of sodium sulphite dissolved in 20 c.c. of water, heat nearly to boiling, and add slowly, with vigorous stirring, one gram of potassium thiocyanate dissolved in 20 c.c. of water. Heat at a nearly boiling temperature for several minutes to coagulate the precipitate and dissolve out all the tartaric acid. Cool somewhat and filter hot, preferably through an asbestos mat on a Gooch filter. Wash well with water and rinse out the suction flask. Then pour through the felt 30 c.c. of a hot 10 per cent sodium hydroxide solution and wash well with water. The assay should be finished hot.

Warm the filtrate to about 50° and titrate, running in the

¹ *J. Ind. and Eng. Chem.* **5** (1913), 215.

permanganate slowly and shaking the flask vigorously. The solution turns green. After about 10 c.c. have been run in, take out a drop of liquid, place it in a drop of hydrochloric acid on a white paraffined plate, and add a drop of 10 per cent ferric chloride solution. If a red color appears, continue to add the permanganate, testing after each 5 c.c. until the red becomes weaker, then test often until the red tint is faint. Add 30 c.c. of (1:1) sulphuric acid, shake until dissolved, and finish the titration. The copper value is .1897 times the iron value. Refer to methods **5c** and **8** for electrolytic modifications of the thiocyanate method. For safety, titrate under a hood.

4a. The Colorimetric Assay. Western Method (after Thorn Smith).—*Standards* for the assay of blast furnace slags are prepared as follows: Take 3 grams of sample of an ore, tested electrolytically, cover it with water, add 10 c.c. of nitric acid (d., 1. 4) and 1 c.c. of hydrochloric (d., 1. 2); heat for a few minutes on a steam bath; dilute with 100 c.c. of water, and then add a slight excess of dilute ammonia. Filter into bottles of uniform size, for comparison of color, and wash until the bottle is filled to the 200 c.c. mark. If the true copper in this sample was .20 per cent, this standard is called B. 2. To prepare B. 3, add .003 gram of copper to another 3 grams of the same sample. B. 4 is prepared by adding .006 gram copper and B. 5 by adding .009 gram of copper, the copper always being added before the ammonia and the samples each treated as with B. 2.

Tailings.—Heat 1 gram of sample on the steam bath with 5 c.c. of nitric acid and a pinch of potassium chlorate; dilute, filter, and wash as in the assay of slags. If the copper per cent by electrolysis was .50, this standard is called T. 5. To prepare T. 6, add .001 gram of copper to another 1-gram sample; .002 gram for T. 7; .003 gram for T. 8; .004 gram for T. 9; .005 gram for T. 10.

Reverberatory Slags.—Take 2 grams of any of the Montana, or Arizona, products, add 10 c.c. of hydrochloric acid and 2 c.c. of nitric acid. Heat, dilute, filter after the addition of ammonia, and wash as in tests of slags from cupolas. If the true copper on this sample was .30 per cent, this standard is called R. 3. To prepare R. 4, add .002 gram of copper to another 2 grams of sample. Add .004 grams for R. 5, and

treat each as in the preparation of R. 3. If samples low enough to furnish the lowest standard are not at hand, remove the copper first by electrolysis from a sample and then add the required amount of pure standard copper solution for the first number in the set.

A set of standards having been prepared for each product as above, another set of bottles is filled almost to the mark with water and 10 c.c. of ammonium hydroxide (.90). A standard solution, containing .001 gram of copper to the c.c., is then run into each from a burette until the color matches the above standards, and the burette reading in each case is carefully noted. The following results were obtained by the chemists. From this table prepare the standards.

BURETTE READINGS FOR STANDARDS

B.2 required 4.4 cc.	R.2 required	3.2 cc.	T.4 required	3.8 cc.
B.3 " 6.7 "	R.3 "	4.6 "	T.5 "	4.7 "
B.4 " 9.1 "	R.4 "	6.1 "	T.6 "	5.7 "
B.5 " 11.1 "	R.5 "	7.9 "	T.7 "	6.6 "
	R.6 "	9.7 "	T.8 "	7.6 "
	R.7 "	11.4 "	T.9 "	8.5 "
	R.8 "	13.2 "	T.10 "	9.5 "

Determination of Copper (in unknown samples). — Treat the blast, reverberatory slags, or tailings, exactly as described above and match the filtrates with the standards, which were prepared by separating the copper in presence of nearly the same interfering elements found in the regular works samples reported to the office for analysis.

4b. Lake Superior Method. — The color test has been superseded by rapid electrolysis in testing slags or tailings high in soluble iron, but is still found useful for the classification of lots of sludges from the diamond drill, and for the rapid assay of Lake mill tailings, and assay slags from the fire assays of native copper products. The permanent standards are diluted from a strong solution to the uniform volume of 200 c.c. by means of dilute ammonia, 1 volume of ammonia (d., .9) to 6 volumes of water. If preserved in thin-walled, cylindrical bottles with tight glass stoppers, the solutions will remain unchanged for about a year. Oil sample bottles will answer but are inferior.

2.5 grams of sample are taken as a standard sample for analysis and also for the set of standards. Dissolve .3 gram

of pure copper in 5 c.c. of nitric acid in a 500 c.c. flask, treat with 5 c.c. of sulphuric acid, boil out the nitric acid, and make the solution up to 1500 c.c. with dilute ammonia as already described. Then 1 c.c. contains .0002 gram of copper.

Fill a burette with the well-mixed solution and run into each standard bottle the amount required to make a set ranging from .1 to 1 per cent of 2.5 grams.

The diameter of the bottles is 4.4 cm. and the height to the 200 c.c. mark, 15.2 cm.

Cupola Slags. — Treat 2.5 grams of powdered slag in a No. 4 porcelain casserole with 7 c.c. of nitric, 7 c.c. of sulphuric acid, and 7 c.c. of water. Warm, and finally boil down to white fumes over a Bunsen burner, stirring to break up any clots and form a paste.

Stir in 50 c.c. of water while still warm and, when the soluble salts are dissolved, add sufficient ammonium hydroxide to precipitate the iron and alumina. Pour the solution through a No. 3 Munktell 15 cm. filter into a bottle of the same volume as the standard set.

Wash the mass with dilute ammonia until the washings appear colorless, and then make the solution up to the 200 c.c. mark with the same dilute ammonia prescribed for the standards. When the bottle is nearly filled, if the tint on shaking appears greener than the standard bottle of about the same depth of color, then complete the dilution with pure water instead of ammonia. If the ferrous oxide is over 10 per cent, the first precipitate of ferric hydroxide should be washed only once, drained, and then washed back into the casserole with a jet of water, using as little as possible. Redissolve the iron in a very little dilute sulphuric acid, precipitate again with a little ammonia, run through the filter into the bottle, and wash until the filtrate is clear.

4c. Color Test of Mansfeld Shales. — H. Koch weighs 2 grams of substance into a small porcelain crucible and roasts the contents on a sand bath, afterwards decomposing the sample exactly as in the electrolytic assay of ore and shales (method 5). From the residue on evaporation, the sulphate of copper is dissolved as usual, then the solution (50 c.c.) with the residue is transferred to a thick-walled, cylindrical glass, 6 to 7 cm. wide and 14 cm. high, which is marked at 250 cm. After the addi-

tion of 30 c.c. ammonium hydroxide (d., .91), it is filled to the mark with water and stirred. After settling, the fluid is passed through a dry 14 cm. filter into a square-cornered bottle with ground sides. The area of the bottle adopted is 60 by 40 mm., the height to shoulder about 70 mm., and the whole contents about 110 cm.; the thickness of the walls must be uniform.

The copper values are ascertained by comparison with standard solutions which are prepared in the central laboratory from shales of known copper content. The copper is usually calculated in kilos per metric ton. The minus error increases with the copper, just as in tests on American ores or slags, hence the standard solutions are prepared according to an empirical scale of perhaps 20 bottles, to read colors from material varying in copper contents from 2 kg. to 140 kg. per ton.

The copper in shales of the usual contents of 25 to 35 kg. (2.5 to 3.5 per cent) is estimated with an accuracy of 1 kg. per metric ton (.1 per cent).

5. Copper by Electrolysis. — In routine work, as observed by A. M. Smoot, the electrolytic assay has advantages over all others, because it is applicable to any sample from refined copper to the lowest tailings; and further, it admits the use of large charges, thus dividing the errors inherent in all such processes, which is an especial advantage with high grade material. This fact is so well recognized that practically no other method is used by large firms for *control* and *umpire assays*.

It is wrong to assume, however, that the copper is thus perfectly separated from other associated elements, and even with the purest refined copper, high results may be obtained by oxidation of the cathode or by occlusion of gases by the deposit. A preliminary separation of copper from associated impurities is sometimes necessary, thus making the electrolysis a finishing process to obtain a weighable deposit.

Chemists are referred to Chapter I for a description of the most convenient apparatus. Perforated cathodes are described in 1, Chapter XI.

Acid Electrolyte. — In Western reduction works, nitric acid is often used alone, particularly with leady ores, if a deposit of lead peroxide is also required, but there is a tendency to oxidation of copper unless the per cent of copper is small and the time of deposition rather short. In accurate work on metallic copper

(Chapter XI), sulphuric acid is therefore added in such amount that when the electrolysis is completed, sufficient free sulphuric acid shall be present to retain arsenic, iron, and other impurities in solution after the greater part of the nitric acid has been reduced to ammonia by the electric current.

5a. Western Assay of Sulphide Ores. — Weigh 1 gram of ore into a beaker (3.5 inches high and 2.25 inches diameter); add 8 c.c. of nitric acid and a little potassium chlorate. Take to complete dryness on the steam bath. Take up with water and 6 to 10 c.c. of nitric acid, fill the beaker with water, allow to settle, and place on the battery. It is often better to use a little sulphuric acid, 2 to 5 c.c., and drive off nearly all the nitric acid, finally adding an exact amount (4 c.c.) of nitric before electrolysis.

5b. Oxidized Ores. — Take a one-gram sample to dryness with 8 c.c. of nitric acid; add 10 c.c. of hydrochloric acid and 2 c.c. of sulphuric acid and take down to fumes of sulphuric anhydride. Dissolve the salts with 8 c.c. of nitric acid and water, allow to settle, and place on the battery.

5c. Mattes. — Moisten a one-gram sample with a few drops of water, add 8 c.c. of nitric acid and 1 c.c. of sulphuric acid, and take to dryness on a steam bath. Dissolve with water and 8 c.c. of nitric acid, filter, and electrolyze. The percentage of silver, as determined by fire assay, is deducted from the percentage of copper plus silver found by electrolysis. 291.66 ounces per ton equals 1 per cent. If the silver is considerable, it may be precipitated with just sufficient dilute hydrochloric acid, avoiding an excess. The silver chloride is filtered off, the traces of hydrochloric acid removed by evaporation and the copper alone deposited by the current.

5d. Western Slags. — Decompose 2 grams in a platinum dish with 6 c.c. of nitric acid, 8 c.c. of hydrofluoric acid, 1 to 2 c.c. of sulphuric acid, and evaporate to white fumes. Take up with water and 10 c.c. of sulphuric acid and place on the battery. Allow about .11 ampere per assay (with a 110-volt current); this gives a potential of 1.4 to 2.3 volts across the electrode terminals of each assay. Finally, test a little of the liquid with a drop of hydrogen sulphide water on a spot plate to prove that the copper has all been deposited. Wash the platinum cathodes first by dropping them very rapidly into a beaker of

water, then by a jet from a bottle. Remove the water by means of 94 per cent denatured alcohol, carefully burn off the slight excess of alcohol (keeping the plate in rapid motion) and then cool and weigh the cathodes.

If the deposits are either slightly grayish, or show dark spots due to arsenic, they may be dissolved in 8 c.c. of nitric acid, or in an acid mixture, and the copper again deposited, removing the electrode just as soon as the process is completed. Copper in ores and furnace products may be separated from bismuth, antimony, and arsenic by precipitation as thiocyanate (3). The white salt is washed thoroughly, carefully ignited in a porcelain crucible, dissolved in 7 c.c. of nitric acid, and the copper estimated by electrolysis as before. Instead of igniting the precipitate, the excess of ammonium thiocyanate may be destroyed by evaporation with nitric acid. Compare also "Eastern methods."

6. Lake Superior Method for Chilled Slags. — If a sample of slag, or other furnace product, is evaporated to fumes with acids, without any addition of hydrofluoric acid, enough copper is frequently retained in the silica to cause a serious error. One of the author's assistants noted that chilled slags, granulated in water, are almost completely soluble in dilute boiling sulphuric acid without separation of silica. The copper is thus taken entirely into solution. Grind the slag to pass through a sieve of 100 meshes to the linear inch (40 per cm.).

Weigh 2 grams of the powder, from which any shot has been sifted out and separately weighed. Transfer from the balanced watch glass to a tall 300 c.c. lipless beaker, 12.5 cm. (5 inches) in height, and 5.7 cm. in diameter. Add 80 to 100 c.c. of distilled water, stirring rapidly until the sample is entirely in suspension. Continue the rapid stirring and add from a graduate 12 c.c. of sulphuric acid (d., 1.84), place over a lamp, and bring to boiling, while stirring to preserve the suspended condition. Boil for about three minutes, and break up any particles of slag which may have settled. The solution should be clear or slightly milky and no more than a trace of silica should remain on the bottom.

Now add carefully three or four drops of nitric acid. A violent effervescence will ensue. As this subsides, and the iron rapidly changes to the ferric state, add 7 c.c. of nitric acid if the copper is to be deposited over night, or 8 to 9 c.c. if the copper assay is to be placed in the Frary rotary device, or in con-

nection with a rotating anode spindle. Dilute to 150 c.c., and electrolyze over night with a current of .8 to 1 ampere per assay, or in the rotary device with 3 to 4.5 amperes. When the copper is nearly deposited, wash down the split cover glasses, and, a few minutes later, test with hydrogen sulphide water on a porcelain spot plate in the usual manner. In the case of yellow solutions, the color of the test should be compared with some untreated solution. Wash the plates rapidly with water and alcohol, ignite, and weigh as in the preceding method. In the Frary solenoid, the deposition of the copper may be completed in 45 to 90 minutes, but the current should not be allowed to act long after the deposition is complete. The solutions must be kept cold, or the copper may commence to redissolve. A solenoid may be cooled by the circulation of cold water between the beaker and copper cylinder, if it is to be kept in continuous operation. The operator should then be able to increase the current to 4.5 amperes per square decimeter, and complete the electrolysis of a sample of waste blast furnace slag in half an hour. Such a method is fairly rapid and far more accurate than any color test.

The platinum cathode is made from a sheet 5 cm. high and 10 cm. wide, giving a total immersed depositing surface of 100 sq. cm., or 1 sq. decimeter, which will be regarded as a *normal area* in the measurement of current density.

UMPIRE AND CONTROL ASSAYS AT THE PORT OF NEW YORK

7. Siliceous Ores.¹ — Such material is generally tested, when *high-grade*, by the same method to be prescribed for high-grade matte. As much as 3 to 5 grams are taken if the ore is *low-grade*. A small amount of copper may be deposited in 6 to 8 hours with a current of .25 ampere. The large samples taken for electrolysis render these methods more suitable for umpire work than the more rapid titrations generally used in the western part of the United States.

8. Heavy Sulphides; Thiosulphate Modification. — Pyritous ores usually contain impurities which would contaminate the copper deposits, and the presence of much sulphate of iron in the electrolyte causes interference, just as it does in the assay of

¹ A. M. Smoot, personal communication.

ferruginous reverberatory or blast furnace slags from native copper. In the case of rich ores, the nitric acid should nearly all be driven out by evaporation; or with impure material, a preliminary separation may be effected by precipitating the copper as cuprous sulphide in the following manner.

Moisten 5 grams of ore with 10 c.c. of water, add 10 c.c. of nitric acid (d., 1.42), and when the action has subsided, 10 c.c. more. Digest the mixture on a steam bath until the ore is decomposed and the sulphur is clean, then boil for a few minutes, cool a little, and add 10 c.c. of sulphuric acid (d., 1.84). Evaporate on a hot plate until the first acid is expelled and white fumes are evolved. Cool, add 150 c.c. of water and 10 c.c. of sulphuric acid. If silver is present, precipitate all of it with sodium chloride, boil, filter, wash the residue with hot water, dilute to 300 c.c., and heat to boiling.

To the boiling liquid, add, drop by drop, a saturated solution of sodium thiosulphate. The ferric iron will be rapidly reduced, and when colorless, the copper will begin to separate as cuprous sulphide. The point at which this begins is easily seen. Add about 2 c.c. of thiosulphate after the copper sulphide begins to form, and boil until the sulphide agglomerates. Filter the hot solution and wash with hot water, or better, hydrogen sulphide water. Dry and ignite in a No. 2 round-bottomed porcelain crucible. Moisten the residue with 3 c.c. of water, add 6 c.c. of nitric acid, and digest for a few minutes; finally, boil, transfer the liquid to a tall beaker and electrolyze for 8 hours or more, according to the per cent of copper, using a current of .25 ampere for cylinders 5.5 cm. wide by 3.8 cm. in height. A better deposit is produced by adding 10 c.c. of sulphuric acid also.

The Thiocyanate Separation of Copper. — This modification is similar to the titration method (3), or the western method for slags, and where antimony is present, is preferable to the thiosulphate, which causes the deposition of at least a part of the antimony. According to A. M. Smoot, treat 5 grams of the ore as above until the filtered solution from the insoluble residue has been obtained. Add ammonia until the liquid is alkaline and then make acid with hydrochloric acid, leaving an excess of about 1 c.c. more than is necessary to dissolve the iron hydroxide. Dilute to 300 c.c., add 50 c.c. of a saturated solution of sulphur

dioxide, and heat on a steam bath until the iron is reduced. Add 3 to 5 c.c. of a solution of potassium thiocyanate (150 grams to 1000 c.c.) and heat again until the precipitate settles. Filter through double papers, wash with warm 2 per cent solution of ammonium nitrate, and proceed as in the thiosulphate method. Compare Western method for slags (5).

9. Roasted Ores, Iron Oxides, and Cinders usually contain copper which is insoluble in acids, even after prolonged digestion. Digest 3 grams of such ores with 25 c.c. hydrochloric acid until the iron oxide is partly dissolved, then add 10 c.c. nitric and boil until only about 5 c.c. remains. Cool, add 5 c.c. sulphuric acid, and evaporate until SO_3 fumes are given off. Cool, add 100 c.c. of water or more, and boil until all soluble salts are dissolved. Add sodium chloride, if necessary; filter and wash the residue with hot water. Transfer the residue to a porcelain crucible; dry, ignite, and fuse it with potassium pyrosulphate. Dissolve the fusion in hot water and filter it into the main solution; or, if the insoluble copper is small, as is usually the case, estimate it separately, colorimetrically. Filter the ammoniacal solution through asbestos, and read the color in 100 c.c. tubes, according to method 4b.

9a. D. J. Demorest claims that a precipitation as sulphocyanate in ammonium tartrate gives a more complete separation from antimony, arsenic, or bismuth, than is possible in sulphuric acid alone. If electrolysis is preferred to titration, the precipitate as obtained is dissolved by repeated treatment on the filter, in a covered funnel, with 18 c.c. of nitric acid (1:2), after which the liquid is boiled 5 minutes under a hood to destroy all the cyanogen compounds before electrolysis. (See 3a.)

10. Eastern Methods for Mattes are the same as those for Western mattes already described. One hundred per cent copper foil is, however, adopted for standards. An operator is justified in using any one of methods 5, 6, 7, 8, 9, that is best adapted to the material treated and the commercial requirements.

11. Copper by Electrolysis in Mansfeld Ores. — For the assay of about 800 shale samples per month,¹ this method is said to offer the advantage that it permits the electrolysis of the unfiltered liquid for copper, the liquid only clarifying by long settling. The procedure is as follows:—A sample of 2 grams of

¹ H. Koch, personal communication.

the fine powdered shale is burned at a dark red heat, in a small porcelain crucible in a Plattner's assay muffle, in order to drive off the bitumens. The roasted mass is transferred to a 150 c.c. beaker, 20 c.c. of a mixture of equal parts of nitric acid (d., 1.42) and sulphuric (d., 1.2) are added and the mixture evaporated to dryness on the sand bath. The cooled mass is taken up in about 70 c.c. of a diluted nitric acid (1:7) with the addition of a few drops of sulphuric acid. The electrolytic precipitation of the copper follows without filtration, employing a small platinum cylinder of 66 sq. cm. total area, and a small platinum wire spiral as anode. As finally placed, the flat spiral wire stands horizontally without touching the glass; the cylinder is fastened to a special tripod stand.

The electrolyses of shales are ordinarily arranged as a set of 16 assays to one working stand, or rack, the strength of current being .1 ampere per assay. When connected at evening, the extraction of the copper proceeds without attention. In the morning, the assay glass is washed with water and the assayer notes whether any copper deposits on the newly moistened portion of the cathode. If this is not the case, the cylinder is quickly withdrawn from the solution, then washed off with water and alcohol, dried in an air bath at 90° C., and weighed on the balance. (A color test by hydrogen sulphide is a more certain indication of the end-point than the one above described.)

Raw Mansfeld Ores. — With ore samples from the deep mines 2 grams are evaporated in a 14 cm. casserole on a sand bath, with 30 c.c. nitric acid (d., 1.2) and 20 c.c. sulphuric acid (d., 1.2) the heat being raised so that the separated sulphur burns. The residue is taken up with about 100 c.c. water and 10 c.c. of sulphuric acid, and then 4 c.c. of a normal solution of hydrochloric acid is added for the separation of silver. After standing 12 hours, the liquid is passed through an ordinary 8 cm. filter into a beaker 15 cm. high and 8 cm. wide, washed with water, and a few drops of sulphuric acid added to render the lead insoluble. The electrolysis of the filtrate (after the addition of 20 c.c. nitric acid and dilution to 400 c.c.) is carried out, generally at night, with the aid of the platinum electrodes already described, and with a current of .3 ampere for each assay. For the estimation of Zn, Ni, and Co, in this material, refer to a later method (3, Chapter VII).

Typolite Ore. — This is treated like ordinary ore (*q. v.*) with the exception of a larger addition (8 c.c.) of $\frac{1}{100}$ normal hydrochloric acid, on account of the higher silver contents. An excess of the acid in this case must be carefully avoided, or the copper will deposit in a spongy form. Current, .3 ampere per assay.

12. Desilverized Residues. — In this oxidized product, containing about 70 per cent copper, it is not necessary to treat in a casserole, to burn off sulphur, etc. Two grams are digested with 60 c.c. nitric acid and 10 c.c. concentrated sulphuric acid until a white anhydrous deposit of copper sulphate is formed. After dilution with water to about 400 c.c., 10 c.c. ammonia is added to lessen the acidity, and the acid liquid electrolyzed with .4 ampere. The assays are usually combined in sets of 3 to 4, but the samples must be similar to insure an equal division of current.

13. Mansfeld Ore Slags. — Five grams of powdered slag are mixed in a casserole with 30 c.c. of nitric acid and 15 c.c. of sulphuric acid and evaporated to dryness on a sand bath. It has been proved that chilled slag is quickly decomposed, while stiff-tempered slag (i.e., gradually cooled) requires an alkali melt. The dry residue is treated hot with 100 c.c. water and 10 c.c. sulphuric acid, then filtered through an ordinary 12 cm. paper into a beaker (15 by 8 cm). The filtrate, after adding 20 c.c. nitric acid, is electrolyzed with platinum electrodes and a current of 0.11 ampere per assay.

14. Typolite Slags. — Two grams are evaporated to dryness with 30 c.c. aqua-regia and 15 c.c. sulphuric acid. The residue is extracted with 100 c.c. of water and 10 c.c. sulphuric acid. The solution, after warming, is filtered into a beaker.

Twenty c.c. nitric acid are added to the filtrate which is then treated with a few drops of cold saturated oxalic acid in order to overcome the harmful effect of the heavy iron contents of this material (40 per cent Fe). Tests are arranged in sets with a current of .3 ampere per assay. The routine electrolyses are carried on over night. It is only in urgent cases that the process is finished in the daytime at the sacrifice of accuracy, in which case the liquids are warmed to 40 to 45° C. The author considers that as the local conditions require a simple assay, the use of mechanical stirrers is prohibited.

Magnetic Separation. — The original ore is peculiar to the

district. A description of the slag produced has been necessarily condensed in the translation of the original paper. Most of the copper contents exist in such slag in metallic form. Some sulphide and silicate are also present, hence it is erroneous to report all the copper as metal. Magnetic separation has accordingly been taken up for the successive mechanical division of the copper, as metal and sulphide, from the silicates. Magnetic treatment is very efficient in consequence of the considerable proportion of magnetic oxide of iron. By a small electro-magnet, connected with six Meidinger elements, pieces of nut size are attracted with ease. The separation can be only approximate as the slag grains will inclose, or be covered with, non-magnetic particles. Nevertheless, four treatments of typolite slag (containing 7.75 per cent copper and .161 per cent sulphur) yielded 15.9 per cent of non-magnetic residue which assayed nearly 33.8 per cent metallic copper and 3.48 per cent copper sulphide.

Method of Assay. — The total copper is determined by the usual methods. For the valuation of the metallic copper only, the most suitable method is the extraction of powdered slag with standard solution of silver nitrate, followed by the dry assay of the silver precipitated by the copper; and as a control, the titration of the silver remaining in the solution by potassium thiocyanate after the Volhard method. The copper sulphide and the metallic iron present (perhaps 1.25 per cent) also take full part in the reaction of the silver nitrate with the metallic copper and only the silicate remains, so that the relative proportions of copper metal, sulphide, and silicate are easily calculated. For a total of 7.75 per cent as noted above, about 6.85 per cent would exist as metal, .58 per cent as sulphide, and .32 per cent as silicate.

NOTE 1. — The magnetically separated copper is itself argenterous. It carries the silver excess of the original typolite slag and a notable amount of gold even after skimming off some half-melted ore which floats on the slag in the descending series of skimming pots at the furnace. The slag copper is enriched with the whole nickel content of the ore, and copper bottoms are formed at the same time in the pots. When this same slag is, however, remelted in a furnace with regulus, the magnetic sepa-

ration of the ground slag is hardly profitable in spite of the high iron content (nearly 38 per cent), for the reason that the iron is then present in the final slag as non-magnetic ferrous silicate.

NOTE 2. — When typolite slag is cooled in the series of pots, it forms zones or layers which increase in magnetic iron oxide towards the bottom and consequently increase in electrical conductivity. If the upper zone contains 1 to 3 per cent copper and 0 to .003 per cent silver, the middle will be twice as rich while the lowest zone will show 4.5 to 5.4 per cent copper and .015 to .017 per cent silver. It was proved by a series of tests that it is impossible to obtain a proper average by ladle samples from the settling pots.

CHAPTER V

ANALYSIS OF ORES, SLAGS, MATTE, AND FLUE DUST

CONTROL OF SMELTING FURNACES

THE methods described in this chapter include only the determinations ordinarily required to furnish the data to metallurgists for regular daily control of furnace operations. Occasional tests for arsenic, bismuth, nickel, sodium, and rarer elements, are reserved for Chapters VI and VII. The methods of this chapter are arranged in the sequence adopted in practical work, rather than in alphabetical order.

Classification. — Furnace material, for the purposes of analysis, may be divided into two classes: — *First*, material decomposed by acids, such as chilled blast furnace slags; *second*, refractory material, leaving an insoluble residue after acid treatment; for example, reverberatory slags, calcined ores, and flue dust. Such a residue evidently requires fusion. The methods are those of the largest western reduction works, except in cases where other methods are specified.

DETERMINATION OF INSOLUBLE MATTER

1. In Raw Ores. — For a special test on Butte ores, refer to the method for sulphur (16). As a general method, heat a half-gram sample in a small beaker, or casserole, for ten minutes with 10 c.c. of hydrochloric acid, add 1 to 5 c.c. of nitric acid (depending on the sulphides present), cover with a watch glass until violent action ceases, then uncover and evaporate to dryness on the steam bath. Sulphides may be treated with 5 c.c. of nitric acid and a little potassium chlorate, 10 c.c. of hydrochloric acid added when the action becomes quiet, and the liquid evaporated to dryness as before. When dry, remove from the bath, add 15 c.c. of hydrochloric acid and 50 c.c. of hot water. Bring to boiling and filter. Wash the insoluble matter with dilute (1:9) hydrochloric acid, then with boiling water.

Fold the filter about the "insoluble," ignite, and weigh. This assay may be combined with the iron titration.

Another operator¹ recommends a first treatment with 7 to 10 c.c. of nitric acid, followed by evaporation to dryness, and cooling. Then add 30 c.c. of (1:1) hydrochloric acid and heat until the solution is as complete as possible. In presence of carbonaceous matter, it may be necessary to bake for a long time, as such residues hold acid very tenaciously.

Roasted Ores. — Digest with hydrochloric acid, without boiling, until the oxidized part is dissolved, add about 3 c.c. of nitric acid to decompose sulphides, and dry as before.

Barium Sulphate Ores. — Treat with 10 c.c. of hydrochloric acid (1:1), boil a few minutes, add 4 to 5 c.c. of nitric acid, and after action has ceased, dry and bake, then proceed as already indicated. After the "total insoluble matter" is weighed, fuse it with sodium carbonate, or mixed carbonates, 8 parts to 1 of residue, digest the fusion with water until disintegrated, filter, and wash. Wash out the crucible with 5 c.c. of hydrochloric acid (1:1) and with this acid dissolve the residue upon the filter, being careful that it is all dissolved and the filter washed out clean. Precipitate the barium as sulphate from a boiling solution, and deduct this barium sulphate from the "total insoluble" to obtain a result defined by custom as "the insoluble residue."

SILICA

2. In Chilled Blast Furnace Slags. — To .5 gram of slag in a small porcelain casserole, add six drops of water and about 3 c.c. of strong hydrochloric acid. Stir well with a glass rod until all lumps are broken up and a smooth jelly results. Now add a few drops of nitric acid and work the jelly up and around the sides of the casserole to a height of about 1.2 cm. This will permit of very rapid dehydration, and will reduce the loss by "spitting." Place the casserole, uncovered, upon the plate and evaporate off all traces of acids, care being taken, however, not to prolong the baking at too high a temperature, or some alumina will unite with the silica and give too high a result when the direct weight of silica is taken; the residue, after ignition, being of a gray instead of a white color.

¹ *Western Chem. and Met.* **3**, 120.

Slightly cool the casserole, add about 20 c.c. of hydrochloric acid (d., 1.20), and boil for a few minutes. Dilute with a little hot water and filter while hot, washing well with hot water until free from chlorides. Ignite and weigh as silica. If exact results, or the percentage of true silica is required, additional precautions are taken as stated in the paragraphs on *ores*.

In a statement of a "co-operative analysis," Thorn Smith¹ has indicated a necessary precaution. At least two evaporations to hard dryness with an intermediate filtration are required to render precipitated silica insoluble in dilute acids. When accurate work is attempted, the silica should finally be ignited ten minutes with the blast lamp.

It is also necessary to correct, in such work, for the small amounts of oxides of iron or alumina, and sulphates of alkaline earths, which remain after treatment of the silica with sulphuric acid and excess of hydrofluoric acid.

The manner of calculation of this correction to the original weight of siliceous residue depends on the forms in which the bases may be assumed to exist in the ignited siliceous residue. Platinum dishes are best suited to accurate work in complete analysis of a slag or ore.

Solubility of Jena Glass.—Thorn Smith and A. M. Smoot have proved that Jena glass, although heat resistant, is easily attacked by alkalis. This undesirable property is due to the presence of oxides or silicates of zinc as a constituent.

Special Solvents.—For complete solution, Smith decomposes Tennessee cupola slags by digestion in a platinum dish with a mixture of hydrofluoric acid and nitric acid. To dissolve the slag for an iron titration only, hydrochloric is substituted for nitric acid.

Another solvent used for ores and slags is the "chlorate mixture" (1 part sulphuric acid, 1 part nitric, and 1 part of a saturated solution of potassium chlorate in nitric acid).

3. In Lake Superior Slags.—Waste cupola slags are chilled by granulation in water at the furnace, the sample dried, then crushed and divided to obtain a 25- to 50-gram sample for assay which will pass a sieve of 100 meshes to the linear inch (39 per cm.). The copper prills, remaining on the sieve, are separately

¹ *Eng. and Min. Jour.* **75**, 295. W. F. Hillebrand, *J. Am. Chem. Soc.* **24**, 362. *Bull.* 422, *U. S. Geol. Survey*.

weighed. In accurate complete analysis, the free iron is estimated by magnetic separation according to the principle outlined in Chapter II, under "Correction for iron from grinder." In some slags this iron contains copper. The total copper is determined most rapidly by method 6, Chapter IV, but may also be estimated in the filtrate from the silica.

Silica.—Dissolve 2 grams of slag in a 300 c.c. casserole by boiling with a mixture of 15 c.c. distilled water, 15 c.c. strong nitric acid, and 10 c.c. of sulphuric acid (d., 1.84) until white fumes appear and the residue, when gently rubbed, has become a smooth paste. Partially cool the residue, then add 90 c.c. of distilled water, wash the glass cover and replace it. Boil for a few minutes until the soluble matter is dissolved, transfer to an electrolytic beaker, and place on the battery stand for the estimation of copper unless silica is the only constituent to be determined, in which case the solution is filtered at once.

For direct estimation of silica, boil the residue with 75 c.c. of (1:2) hydrochloric acid, decant through an 11 cm. filter placed in a platinum cone over a suction flask. Then boil the residue with 50 c.c. of (1:1) hydrochloric acid to extract calcium sulphate, dilute to 75 c.c., filter, wash, ignite, and weigh. Treat the residue with hydrofluoric acid and one drop of sulphuric after moistening with water. Ignite and reweigh. Fuse with potassium pyrosulphate, dissolve, and add to main solution. If a test for barium is advisable, separate it from the original residue by fusion with sodium carbonate and proceed as in method 1, under the head of "Barium Sulphate Ores."

SILICA IN REFRACTORY MATERIALS

4. In Reverberatory Slags (also Calclines, Briquettes, and Flue Dust).—Such material yields an insoluble residue requiring fusion. Reverberatory furnace slag, from smelting of ores, contains such a small amount of copper that it can be fused without any preliminary treatment.

With other refractory products, weigh .5 gram, place in a small casserole, and add 6 c.c. of hydrochloric acid and 3 c.c. of nitric acid. Cover the casserole, heat for a few minutes on the hot plate, bring to boiling, dilute with boiling water, and filter

through a fine paper into a larger casserole. Wash the residue on the paper three times. Fold the filter about the residue and ignite it in a cup or crucible. Place the filtrate on a hot plate while the fusion is being made. To fuse the slag or ignited oxides, mix them well with 6 to 8 grams of anhydrous sodium carbonate in a platinum crucible (or a dish if preferred), and then cover the mixture with 1 or 2 grams of sodium carbonate. Place on a scorifier, preferably, and fuse in a muffle. Raise the heat gradually from dull to bright red, and keep at a red heat for 15 minutes. Dip the crucible in water to cool. Partly fill with water and warm for a few minutes on a hot plate. The cake, as a rule, can be loosened from the crucible by this treatment. Wash it into a casserole containing the main solution which has already been evaporated to dryness. Cover, then add 10 to 30 c.c. of hydrochloric and 1 c.c. of nitric acid. If the fusion was made in a dish, cool, add water, then add 10 c.c. of hydrochloric acid and warm until the contents can be easily transferred to the original casserole. If the color of the fusion indicates the presence of much manganese, it must be removed from the dish without the use of acid, as there is danger of liberation of chlorine.

Evaporate the contents of the casserole to complete dryness again, but do not bake long above 115° C., as some silica is liable to recombine with the alumina.¹ When dry, remove from plate, add 10 c.c. hydrochloric acid and 30 c.c. of water, and boil for a few minutes. Filter, wash ten times, ignite, and weigh. Test the residue for purity, by the usual treatment with hydrofluoric acid, and ignition. For very accurate results increase the sample weight.

ALUMINA

5. Alumina in Ores and Slags.—Decompose the sample, dehydrate, and filter off the silica as in the silica determinations. Purify the silica by evaporation with a drop of sulphuric acid and excess of hydrofluoric acid and fuse the residue with a little potassium pyrosulphate, if necessary, to bring it into solution. In the filtrates, determine the alumina by the **Western phosphate method**, to be described.

¹ *Methods of Rock Analysis*, by W. F. Hillebrand; also *J. Am. Chem. Soc.* 24, 362, and *Bull.* 422, *U. S. Geol. Survey*.

Instead of treating with hydrogen sulphide, ferric hydroxide and alumina may be precipitated with ammonia. The mass is dissolved in hydrochloric acid, the solution diluted to 400 c.c., and the alumina precipitated as before. This serves to separate the alumina from the small amount of copper contained in such waste ore slags. The other metals affected by hydrogen sulphide are usually present in such small quantities that they may be neglected. In making the ammonia separation, a large excess of ammonium chloride must be present and the solution boiled for fifteen minutes to break up any aluminates which may have been formed.

Precipitation. — After the excess copper has been removed, dilute the acid filtrate from the silica with cold water to about 400 c.c., add 30 c.c. of a 10 per cent solution of ammonium phosphate, and then dilute ammonia until a slight permanent deposit forms. Now add 1.5 c.c. concentrated hydrochloric acid and 40 c.c. of a 20 per cent solution of sodium thiosulphate and heat to boiling. When boiling has continued a couple of minutes, add 15 c.c. of a 20 per cent solution of ammonium acetate and 6 c.c. of strong acetic acid, and boil about 15 minutes longer. This addition of ammonium acetate and acetic acid after boiling gives a much more granular precipitate, which, after allowing it to settle for about 20 minutes and decanting the clear supernatant fluid, filters very rapidly. Wash with hot water ten times, dry, ignite gently at first, and weigh as Al_2O_3 , P_2O_5 — 41.85 per cent of which is alumina (Al_2O_3).

Instead of the previous method, the following plan may be adopted for the removal of the copper and similar metals. Should metals affected by hydrogen sulphide be present, add ammonia to the filtrate from the silica until the liquid is nearly neutral, then add 2 or 3 c.c. of hydrochloric acid in excess, reduce the solution with sodium sulphite, and boil off the excess of sulphur dioxide. Add 15 c.c. of hydrochloric acid, pass hydrogen sulphide through the solution, filter off and wash the sulphides with cold water. Boil off all hydrogen sulphide from the filtrate, dilute to 400 c.c. with cold water, and proceed as before.

IRON OXIDES

6. Direct Titration of Ores. — Oxidized iron ores (carrying copper) often dissolve more rapidly if a little stannous chloride

is added with the hydrochloric acid. If the tin solution is added to aid the solution of the iron, then the reduction of iron before titration must be made with stannous chloride (as tin interferes with a solution reduced with lead), or an excess of mercuric chloride should be added to the solution after decanting from lead.

To the filtrate, add 5 to 10 grams of test lead and boil until colorless. Decant from the lead (filtration often being necessary), and wash the lead very thoroughly. Cool, add 10 c.c. of hydrochloric acid, and titrate with potassium bichromate, if preferred. If the solution appears yellowish after decanting from lead, add 2 drops of stannous chloride solution and mercuric chloride in excess before titration. When copper, arsenic, and antimony are absent, heat the filtrate from "insoluble" nearly to boiling, reduce as before, cool, and titrate. Separation of iron from copper by ammonia is not complete in one treatment, however. The ferric and aluminum hydroxides, with the filter, are placed in a beaker, 50 c.c. of boiling water added, and the solution titrated as already described. If care is taken not to add the stannous chloride in large excess, the mercuric chloride may be added to the hot liquid. It is then diluted with cold water and titrated. If a large excess of stannous chloride is added by accident, run in potassium permanganate solution from a burette until the iron solution is a pale yellow; add one or two drops stannous chloride in excess, then mercuric chloride, and proceed as before.

7. Lake Superior Method. — Dissolve 2 grams of sample in acids, evaporate to fumes with 10 c.c. sulphuric acid and dilute. (See method 5, Chapter IV.) Two precipitations of iron by ammonia do not effect a complete separation. The copper may be very rapidly and exactly removed by placing the solution in an electrolytic beaker (see electrolytic assay of copper), and passing 3 to 4.5 amperes of current through the solution after placing the beaker in a Frary solenoid, or rotary device. To get a bright deposit, add 5 to 8 c.c. nitric acid and keep the solution cold. When testing for the end-point of electrolytic deposition, preserve the test portion, and return it to the main solution after the plate has been withdrawn. The sulphur should first be destroyed by heating the test portion with a little potassium permanganate. The time of electrolysis for a 2-gram sample is 30 to 60 minutes.

For the exact estimation of iron it is necessary to filter the original solution (or electrolyte) and decompose the washed insoluble matter by fusion. Combine the two solutions, oxidize the iron, precipitate twice with ammonia, redissolve the iron in 10 c.c. hydrochloric acid (1:1), and wash the paper. Reduce as above, destroying the slight excess of stannous chloride by the addition of 5 c.c. of a saturated solution of mercuric chloride. Dilute to 400 to 500 c.c. and titrate with potassium permanganate (39, Chapter III). Add 10 to 20 c.c. of titrating solution **25** to prevent the formation of a yellow iron coloration. One c.c. of permanganate oxidizes about .01 gram of iron, Fe.

If a test of the electrolyte is to be made for iron only, it may be evaporated to fumes to remove nitric acid.

Add 30 c.c. of water and 10 of hydrochloric acid, heat to boiling, then add sufficient potassium permanganate to produce a yellow color and destroy a trace of sulphur. Reduce as before and titrate, after dilution with cold water to 400 c.c. Calculate to the compound in which the iron exists in the ore.

8. Iron in Slags. — The percentage of iron oxide, FeO , is found by titration of a 0.5 to 2 gram sample. Chilled waste slags from Lake Superior furnaces may be dissolved as directed in method **3** for silica, and the copper removed by rapid electrolysis. Boil the solution down to white fumes after electrolysis to remove nitric acid.

Add 30 c.c. of water and 10 c.c. of hydrochloric acid, heat to boiling, and add a little potassium permanganate, if necessary, to color the solution yellow and destroy any sulphur compound. Reduce and titrate as with ores. For ordinary furnace tests it is not necessary to remove the copper. Proceed as in the next paragraph.

Ore slags, from the blast furnace, are dissolved in a similar manner. To .5 or 1 gram of slag in a beaker, add about 50 c.c. of boiling water, and then while stirring to keep the slag in suspension, pour in 10 to 15 c.c. of hydrochloric acid (d., 1.2). Boil for a few minutes until the solution clears (any slight residue of coke dust being neglected). Oxidize to yellow color with permanganate. Reduce with stannous chloride in very slight excess, followed by mercuric chloride in excess as already mentioned in **6**, and titrate with either potassium bichromate, or permanganate, as preferred.

With the dichromate, use potassium ferricyanide as an indicator, placing the test portions in contact on a white spot plate.

CALCIUM AND MAGNESIUM

9. Direct Method for Lime. — Precipitation of calcium oxalate in *oxalic acid* solution, in presence of the other bases, is used in the western States as a special test for lime only.

To the filtrate from the silica, add ammonia in excess and then oxalic acid, little by little, until the hydroxides just dissolve. Make the solution slightly alkaline once more, and then redissolve the iron by adding oxalic acid in slight excess. The solution should now be of a light apple-green color. Boil well for a few minutes, filter, and wash well with hot water until free from oxalic acid, — six or seven times usually being sufficient. Drop the filter and calcium oxalate into a beaker containing 150 c.c. of boiling water. Add 10 c.c. of dilute (1:1) sulphuric acid and titrate at once with potassium permanganate (solution 40, Chapter III). The permanganate may be standardized with chemically pure sodium oxalate which should be dried at 100° C. before use and preserved in a small glass-stoppered bottle. $\text{Na}_2\text{C}_2\text{O}_4 \times .41843 = \text{CaO}$. Correct sodium oxalate may be obtained from the U. S. Bureau of Standards.

10. Calcium and Magnesium (in chilled cupola slags). — To the filtrate from a silica determination add an excess of ammonia and 5 grams of ammonium chloride (prepared from chemically pure reagents), then 10 c.c. of bromine water and about .1 gram of ammonium persulphate, as in the "Estimation of zinc," 15, Chapter VII. Bring to a boil, filter, dissolve the precipitate in dilute hydrochloric acid, add bromine water and ammonium persulphate as before, heat to boiling and filter again.

After washing the hydroxides, precipitate the calcium (in the combined filtrates from iron, alumina, and manganese), with ammonium oxalate, using .5 to 1 gram of the dry salt or 20 c.c. of the saturated solution. Filter, wash well, and in the filtrate, separate the magnesia by stirring five minutes with an excess of ammonium phosphate (6 and 51, Chapter III). Have the solution strongly ammoniacal with about one-fourth its volume of ammonium hydroxide (d., .90) to prevent the precipitation of zinc. Dissolve the precipitate in a very small amount of hydrochloric acid, add a small crystal of the phos-

phate, then ammonia drop by drop, until alkaline, stirring vigorously. Wash with dilute ammonium hydroxide (1:10) containing 10 per cent of ammonium nitrate, ignite gently at first, and weigh when cooled. Magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, $\times 0.36207$ equals magnesium oxide, MgO .

In the absence of manganese, omit the bromine water and persulphate. In some Lake Superior slags which contain much lime, the calcium oxalate should be dissolved and reprecipitated to obtain a perfect separation from magnesium salts. About 75 c.c. of water and 5 c.c. of sulphuric acid are finally used to dissolve the calcium oxalate for titration. Place the filter and contents in the original beaker, cover with the dilute acid, and heat nearly to boiling. A few drops of manganous sulphate in the solution causes the permanganate to act more quickly.

11. Calcium and Magnesium (in reverberatory slags and ores). — Precipitate hydroxides with ammonium hydroxide and wash six times, then dissolve in dilute hydrochloric acid and titrate the iron.

The calcium oxide in these refractory samples is usually below 6 per cent, and only .2 to .4 per cent of calcium oxide would be recovered by redissolving and reprecipitating the hydroxides. With higher percentages, a second separation with ammonia must be made even in routine technical work. Rich oxidized slags from Lake Superior furnaces treating concentrates of native copper, often contain as much as 5 per cent of free shot copper which must be separated and weighed during the grinding and sizing of the 25- to 50-pound sample. The insoluble portion of the slag is fused, preparatory to analysis for bases. After the slag has been totally decomposed with the exception of silica, the bases are determined as customary with blast furnace slags.

Magnesium is determined by precipitation with phosphates, as in (10).

12. Sodium and Potassium Oxides. — The determination of these elements is seldom necessary in furnace control. Refer to Chapter VII (6, 7, 9).

SULPHUR IN CRUDE PRODUCTS

Principle. — Sulphur, or sulphate, is usually estimated by oxidizing the sulphur to sulphuric acid, then precipitating with barium chloride in a pure hydrochloric acid solution.

Lake Superior copper deposits contain but a trace of sulphur, excepting in a few small cross-veins. The Western methods, to be described, are the same as those used in the eastern States and Europe for all furnace products.

13. Sulphur in Roasted Ores.—Treat .5 gram, or $\frac{1}{2}$ the sulphur weight (.687 gram), with 10 c.c. of a mixture of nitric acid and potassium chlorate. Evaporate to dryness on a steam bath. Take up with 5 c.c. of hydrochloric acid and 15 c.c. of water. Boil for a few minutes and filter off the insoluble matter. Bring the filtrate to a boil, add barium chloride solution, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, using an amount equivalent to 1 gram of the crystals for calcines and 2 grams for ores. Allow the barium sulphate to settle, filter, and wash 6 to 10 times with boiling water. Dry, ignite at a dull red heat, and weigh the cooled crucible and barium sulphate. Barium sulphate $(\text{BaSO}_4) \times 0.13735 = \text{sulphur (S)}$.

If accurate work is required, the solution must be repeatedly evaporated with excess of pure hydrochloric acid in order that the solution may be free from all nitrates and chloric acid before the sulphuric acid is precipitated.

To avoid errors which are introduced by direct precipitation in presence of iron, proceed as follows: After repeated evaporations with hydrochloric acid, dissolve in the dilute acid and filter. Heat the filtrate nearly to boiling, make ammoniacal, and then add an excess of barium chloride. Now make the liquid slightly acid with dilute hydrochloric acid, allow to settle in a moderately warm place, but do not boil. Filter, wash very thoroughly, dry, and ignite. Good results in presence of iron may also be obtained by adding the barium salt in a cold solution and allowing to stand, cold, for 12 hours before filtration. Compare with the semi-electrolytic method, 20.

14. Sulphide Ores and Matte.—Add 10 to 15 c.c. of nitric acid (d., 1.36) to a .5 gram sample. Place on the front of the hot plate and add small quantities of potassium chlorate at frequent intervals. When the sulphur is all in solution, remove the watch glass and evaporate to dryness. Then proceed as in the previous method.

The solution of sulphur in some mattes is difficult and requires prolonged treatment with nitric acid and potassium chlorate. The following scheme may hasten matters in such

cases: Sprinkle 1 gram of potassium chlorate on .5 gram of sample, add 10 to 15 c.c. of water, and bring to a boil. Add 10 to 15 c.c. of nitric-chlorate mixture and heat to boiling, keeping the solution well covered until all the sulphur is dissolved. Remove the watch glass, evaporate to dryness on the steam bath, and proceed as before.

One gram of barium chloride crystals will precipitate 23.4 per cent of sulphur on a half-gram sample, and may be added in solution. The purest barium sulphate is obtained by having the solution of sulphates very dilute, with only a few c.c. of hydrochloric acid in excess, and by adding the barium chloride drop by drop, while stirring.

15. With Sulphates. — For the determination of total sulphur in ores containing barium sulphate or large quantities of calcium sulphate, one may employ a fusion method (sodium carbonate and potassium nitrate) with sodium chloride.¹

16. Sulphur in Lead Ores. — Proceed as before, after evaporation to dryness. Take up the residue with 5 c.c. of hydrochloric acid and 5 grams of ammonium chloride and 15 c.c. of boiling water. These reagents, on boiling, will dissolve any lead sulphate which may have formed during evaporation.

17. Sulphur in Ores Carrying Zinc. — Beckman's method consists in fusing .5 gram of ore with 25 grams of a (6:1) mixture of sodium carbonate and potassium chlorate. The sintering process of Waring for heavy zinc ores is of a similar nature.

18. The Sintering Process of F. G. Hawley is more simple than that of Waring. For decomposition, mix .5 gram of ore thoroughly with six to eight times its weight of a mixture of zinc oxide and sodium carbonate (4:1); sinter at a low red heat for 15 minutes in a porcelain crucible, leach with warm water, and filter.

Acidulate the filtrate with hydrochloric acid, add 5 c.c. in excess, and add by degrees to the boiling solution a sufficiency (about 20 c.c.) of a semi-saturated solution of barium chloride. Slags may be similarly treated.

19. Sulphur in Heavy Pyrites. — The next two modifications are two new devices of New York chemists for the solution of rich copper-bearing pyrites and for the elimination of the injurious effect of ferric chloride. (Compare method **13**.)

¹ Fresenius, *Quantitative Analysis*.

Allen and Bishop¹ recommend solution in a mixture of bromine and carbon tetrachloride, and reduction by powdered aluminum as follows:

1.3735 grams of ore are placed in a dry 300 c.c. Jena beaker, 10 c.c. of a mixture of 2 parts of liquid bromine and 3 parts of carbon tetrachloride by volume are added, and the covered beaker shaken gently for 15 minutes at room temperature. Then 15 c.c. of nitric acid (1:4) are added and the mixture allowed to stand 15 minutes longer, after which the beaker is heated up gradually on the steam bath and the solution taken to dryness. Ten c.c. of hydrochloric are next added, the solution evaporated again, and the silica thereby dehydrated. Filter and reduce the ferric chloride by gradual addition of powdered aluminum, free from sulphur. Precipitate the barium sulphate in the cold by adding a 5 per cent solution of barium chloride at the rate of 5 c.c. per minute, the total volume of the solution being 1600 c.c.

20. Semi-electrolytic Method for Sulphur.—The next method quoted is more accurate than 19, because the volume of the solution is kept very small, thus favoring higher results, and the interfering metals are nearly all eliminated from the solution.²

The ore should be ground *just* to pass a sieve of 80 meshes to the linear inch. .5 gram of dried ore (or .687 gram = $\frac{1}{2}$ factor weight) is placed in a 250 c.c. beaker with a mixture of 3 parts nitric acid (d., 1.42) and 1 part of hydrochloric acid to which 4 or 5 drops of bromine have been added. Cover the beaker tightly, and allow it to stand at room temperature for one half-hour. Transfer to a steam bath, heat gently until action ceases, then raise the cover, and evaporate to dryness. Add 5 c.c. of hydrochloric acid to the residue, heat until action ceases, wash the cover, and evaporate to dryness. Treat with hot water until residue is disintegrated, and wash the solution into an electrolytic beaker, containing a mercury cathode with insulated wire connection. Dilute to 75 c.c., pass a current through a platinum spiral anode to the mercury for 5 to 6 hours at .8 to 1 ampere, or at a lower rate overnight. All metals pass into the mercury.

Siphon, or pour off, the colorless liquid, wash by decantation four times with 25 c.c. of water, then pour off mercury into

¹ *Eighth Inter. Congress of Appl. Chem.* **1**, 38.

² A. M. Smoot, *Eng. and Min. Jour.* **94**, 412; *J. Am. Chem. Soc.*, **25**, 911.

small beaker, and wash the beaker once (especially the lip) with water. Filter into an 800 c.c. beaker and wash 4 to 5 times with hot water. Dilute to 450 to 600 c.c., heat to boiling, and add to boiling liquid 25 c.c. (or 34 c.c. for .687 gram ore) of a 10 per cent solution of barium chloride in a thin stream. The barium sulphate contains impurity amounting to .06 per cent to .09 per cent on .5 gram of pyrites, but the correction for solubility nearly balances this, leaving a final plus error of .01 to .04 per cent of sulphur, as calculated.

The objection to this method for a large amount of work is the necessity for electrolysis and the treatment and purification of all the mercury. It seems well adapted to umpire assaying. Compare method **13**.

CHAPTER VI

SPECIAL ELEMENTS IN ORES, SLAGS, AND MATTE

ARSENIC

1. Distillation (*Method of Skinner & Hawley*). — A distilling solution is required. (a) Dissolve 300 grams pure cupric chloride crystals in one liter hydrochloric acid (d., 1.20) (solution 17, Chapter III). (b) Dissolve one pound (453.6 grams) zinc (free from arsenic) by adding to it gradually a mixture of 1250 c.c. hydrochloric acid (1.20) and 500 c.c. of water. When the zinc has dissolved, evaporate the solution to 1100 c.c. (solution 58, Chapter III). Mix (a) and (b). The principle on which the assay depends is the evolution of arsenious chloride directly from the sulphide by distillation in a saturated solution of chlorides of copper and zinc.

Analysis. — Add 5 c.c. nitric acid to a half-gram sample in a small beaker. (A little potassium chlorate is added with flue dust samples. If desired, Low's method of decomposition may be used as described in method 7.) When the action becomes quiet, add 6 to 10 c.c. hydrochloric and evaporate to complete dryness on steam bath. As there is danger of loss, the temperature should be low. Take up with 5 c.c. hydrochloric acid and 25 c.c. of water. Bring to a boil and filter off the insoluble matter. Dilute the filtrate to 200 c.c. with boiling water. Add sufficient sodium sulphite to render the solution colorless. Boil off the excess of sulphur dioxide and add 15 c.c. hydrochloric acid. Pass a current of hydrogen sulphide through the solution until it is saturated. Filter off the precipitated sulphides, wash out the iron salts, and place the sulphides in a flask connected to an 8-inch (20 cm.) Allihn condenser, with large straight bulb tube, set vertically. Never allow the lower end of condenser to be more than sealed by the water in beaker (200 c.c.). Add 50 c.c. of "distilling solution" and distil carefully until the thermometer reads 115° C. Remove the flask from the heat and

add 25 c.c. of hydrochloric acid. Distil again until the thermometer reads 115°C . Pour distillate into a No. 3 beaker, make alkaline with ammonia (about 25 c.c. being required), just acidify with dilute hydrochloric acid. Cool, add 2 to 4 grams of bicarbonate of soda and a little starch solution, and titrate with standard iodine solution. (Use 20, Chapter III.) On samples low in arsenic, 1 to 5 grams of sample may be taken.

Rapid and complete precipitation of arsenic, in samples containing only small quantities of other hydrogen sulphide metals may be affected by adding 100 mg. of pure copper to the sample. Antimony and tin may be estimated in the residue from distillation.

2. In Slags (*Skinner & Hawley*). — Treat 5 to 10 grams with 10 c.c. nitric acid, 10 c.c. hydrofluoric, and 2 c.c. sulphuric acid. Evaporate to sulphuric fumes. Take up with 10 c.c. hydrochloric acid and 25 c.c. water, then boil and filter. Dilute filtrate to 500 c.c. Almost neutralize with ammonia. Reduce with sodium sulphite and proceed as before. Hydrofluoric acid is not necessary in the case of chilled slags.

3. Sintering Method (*F. G. Hawley*). — Mix .5 to 1 gram of ore with six to ten parts of an equal mixture of zinc oxide and sodium carbonate. Sinter in a porcelain crucible for 15 to 20 minutes. Start at a low red heat and increase to full redness. Leach with hot water and filter. Boil solution carefully, neutralize with nitric acid, and add just 4 drops excess, using litmus paper as an indicator. See that any alumina or zinc oxide, that may have run through the filter, is dissolved. Boil the solution to remove carbonic acid gas, remove from the hot plate, and add a solution of silver nitrate. Seven-tenths gram of silver nitrate is sufficient for .1 gram of arsenic. No red precipitate should be visible. If any appears, add a few drops of nitric acid until dissolved. Now add about 1 gram of sodium acetate, and stir rapidly. Let stand for 20 minutes, filter, and wash. Dissolve the silver arsenate through the filter with dilute nitric acid, dilute the solution, and titrate with a standard solution of ammonium thiocyanate, using ferric sulphate as an indicator. (Solution 8, Chapter III.)

4. Evolution as Arsine¹ (*Modification of Cobeldick*). — For

¹ F. W. Schmidt, *J. Anal. and Appl. Chem.* (1892), 408; Heath, *Eng. and Min. Jour.* **63**, 663.

determination of *traces* of arsenic, 2 grams of ore are weighed into a 150 c.c. beaker, 10 c.c. of strong nitric acid added, covered with a watch glass, and allowed to digest all night in a warm place. The liquid is diluted to 100 c.c. and excess ammonia added, boiled, cooled, filtered, and washed in cold water. The hydroxides are dissolved in dilute sulphuric acid (1:10), evaporated dry, and fumed on a silica plate. The mass is taken up with water, and a little sulphuric acid if necessary, the bulk of solution being about 50 c.c., warmed to dissolve all soluble matter and transferred to a Marsh apparatus which is generating hydrogen from pure zinc and sulphuric acid or hydrochloric acid. (A better reduction is secured by adding, also, .5 c.c. of 80 per cent solution of stannous chloride.) The arsenic mirror is concentrated in the constricted portion of the tube and is compared with standard mirrors made with known amounts of arsenic brought into the solution (in presence of a trace of iron salt). If the material contains more than .1 per cent of arsenic, the portion of the tube containing the mirror is cut off, weighed, the tube cleaned, and reweighed. (Ericsson proposes to conduct the gas through .1 normal silver nitrate, add excess hydrochloric, filter, neutralize, and titrate with .002 normal iodine solution.) Antimony reacts also, if present.¹

Gutzeit Test.—Allen & Palmer have recently presented a modified Gutzeit test which may be useful for continuous work in the estimation of traces of arsenic.²

5. Nitrate Fusion.³—Fuse 1 to 5 grams of the ore with six to ten times its weight of an equal mixture of sodium and potassium nitrates, and precipitate the arsenic from the aqueous solution with silver nitrate. The crucible is, however, considerably attacked.

6. Semi-fusion with Potassium Bisulphate.—The following method of A. H. Low⁴ is remarkably accurate for ores which can be thus decomposed. The first, or distillation, method is so much quicker that it seems to be preferred in the largest works, although it may be combined with the method of solution described in the next paragraph.

¹ *Svensk Farm. Tidskrift*, **18**, 473 (1914).

² *Eighth Inter. Congress Appl. Chem.* **1**, 9.

³ Method of Dr. R. Pearce.

⁴ *J. Am. Chem. Soc.* **28**, 1715.

Digest .5 gram of ore with 7 grams potassium bisulphate, .5 gram tartaric acid, and 10 c.c. strong sulphuric acid, to a clear melt, sulphur-free. After cooling, the melt is dissolved in 60 c.c. of (1:5) hydrochloric acid with 2 to 3 grams tartaric acid, diluted and treated with hydrogen sulphide. Sulphides are dissolved in potassium sulphide and filtered into a 300 c.c. flask. Three grams bisulphate and 5 c.c. sulphuric are added, the mixture boiled down again, cooled, and taken up with 75 c.c. of (2:1) hydrochloric acid and hydrogen sulphide passed again. Moisten the filter with acid of the same strength, and wash with the mixture. The arsenic is now on the filter, and antimony and tin should be in the filtrate. From this point the three are treated separately. First, the arsenic is determined by dissolving the sulphide in a little ammonium sulphide, washing into a 300-c.c. Jena flask, and reducing with complete expulsion of sulphur by boiling vigorously with 2.5 grams of potassium bisulphate and 5 to 10 c.c. of sulphuric acid (d., 1.84). Titrate the cold aqueous solution of the paste by iodine as directed for "arsenic in copper," Chapter XII. Use iodine solution 20, Chapter III.

It is necessary to boil the solution in the Jena flask very hard, after the water is expelled, in order that the acid fumes may carry all sulphur out of the neck of the flask. The solution should be titrated within a few hours after reduction. One cubic centimeter of iodine = .005 gram arsenic.

ANTIMONY

7. Antimony in Ores is finally estimated, according to Low, by diluting the filtrate from arsenic (6) with four parts of water, separating the antimony as sulphide by treatment with hydrogen sulphide, and reducing by digestion in a Jena flask, in the same way as for arsenious sulphide, but with double the quantity of potassium bisulphate and sulphuric acid. Expel all the sulphur and most of the free acid, cool, add 50 c.c. of water and 10 c.c. of hydrochloric acid. Dilute to 200 c.c. with cold water and titrate with standard potassium permanganate. Multiply the iron value by 1.0751, or the oxalic acid value by .9532 to obtain the titer for antimony.

8. Antimony may also be estimated by dissolving the ores, or slags, etc., in a mixture of acids, filtering and fusing any

residue with carbonates and nitrate of sodium, then separating the arsenic and antimony from the precipitated sulphides by treatment with dilute sodium sulphide solution. Evaporate the alkaline solution to dryness on the water-bath or steam plate. Then oxidize the sulphur by digestion with red, fuming nitric acid, evaporate to dryness again, and dissolve the salts in 25 c.c. of water, or more. Add an amount of hydrochloric acid (d., 1.2), equal to twice the volume of the solution of the arsenic group, and precipitate the arsenic alone by hydrogen sulphide. Filter, testing the filtrate again. Wash with acid of the same strength. Then dilute the filtrate with 4 parts of water and precipitate the antimony, and tin if present, observing the precautions of method 3, Chapter XII. Antimony may likewise be dissolved out of the mixed sulphides as in 10. Tin may also be separated from antimony according to method 11, the arsenic having been previously removed as just described.

9. Antimony by Electrolysis.—Simple ores are decomposed by digestion with acids or by Low's process. Refractory ores may be decomposed, after Hawley's formula, by mixing 1 to 2 grams of ore with 8 to 10 parts of a (1:1) mixture of sodium carbonate and flowers of sulphur and heating slowly in a covered porcelain crucible for 15 minutes, finishing at a moderate red heat. Cool with the cover on, leach with hot water, and boil for five minutes. If the precipitate does not settle readily, or the solution appears green, add 2 to 4 grams of sodium sulphite, and boil again. Make up to 200 c.c. and pass through a dry filter into a dry beaker. Remove 100 c.c. to a 300 c.c. beaker, acidify with acetic acid, using 10 c.c. in excess, and boil for one minute.

For accurate work, the filtered sulphides should be dissolved in ammonium sulphide (or sodium and potassium sulphides in presence of copper), and precipitated a second time with acetic acid.

The antimony may be dissolved out by boiling (1:1) hydrochloric acid and titrated, ignited with nitric acid in a porcelain crucible and weighed, according to Fresenius, as tetroxide, — or the compound may be electrolyzed, — if the antimony is present in quantity.

Electrolysis.—Dissolve the sulphides in 15 c.c. of sodium monosulphide (solution 52). W. B. Price recommends a solution of 1.18 specific gravity, or density. Dilute to 70 c.c., add

3 grams of potassium cyanide, and electrolyze in a Frary rotary apparatus (or solenoid), with a current of 6 amperes and an electrode tension of 4 volts.

TIN (WITH ARSENIC OR ANTIMONY)

10. If Tin is present in quantity, evaporate the filtrate from arsenic to dryness on the steam plate after adding enough potassium chloride to form a double salt with the tin and antimony. Redissolve by boiling for one hour, if necessary, with a mixture of 5 grams of ammonium oxalate and 5 grams of oxalic acid dissolved in 100 c.c. of water (a solution proposed by G. W. Thompson).

Precipitate the antimony from the hot liquid by gaseous hydrogen sulphide and filter the hot solution. Dissolve the sulphide in a very little hot dilute sodium sulphide, pour into a boiling solution of half the former quantity of the oxalic mixture, and repeat the precipitation and filtration. Boil out the hydrogen sulphide, and electrolyze the combined filtrates for tin. The solution should be kept in circulation by a slow stream of air, or by a revolving anode.

Time 2.5 hours, and current .8 ampere per sq. decimeter. This procedure gives a much better separation of tin and antimony than is possible with the original method of Clarke. Refer to the special volumetric method, 12, Chapter VII and to "Antimony," Chapter XII.

BISMUTH

11. Combination Assay. — An approximate test of ores and slags may be made by fire assay as for lead, adding enough pure lead to obtain an average button. This button is then flattened, dissolved in dilute nitric acid, the solution made up to a definite volume with dilute sulphuric acid, shaken, and a known portion quickly filtered through a dry filter into a calibrated flask, and subsequently evaporated to fumes of sulphur trioxide. The "density" of the lead sulphate is taken as $4\frac{4}{9}$ nearly, or the volume of the sulphate from 75 grams of lead = 16.875 c.c. (L. G. Eakins).

The volume of the lead precipitate is deducted from the total volume. After the residue from evaporation has been taken up with water, any lead sulphate is filtered out, hydrogen sulphide is passed in for 10 to 15 minutes, the sulphides filtered off, and

extracted with yellow potassium sulphide. Dissolve the insoluble sulphides in fuming nitric acid, and evaporate again with 3 to 5 c.c. of sulphuric acid. Filter and wash again, make the liquid slightly alkaline with sodium carbonate, and add a few drops of potassium cyanide. Boil, allow to settle, filter on a fine paper, wash with warm water, and redissolve in a little nitric acid. Finally, separate the bismuth by precipitation with an excess of ammonia and ammonium carbonate, ignite very carefully in a porcelain crucible at a low red heat, avoiding undue reducing conditions, and weigh as bismuth sesquioxide, Bi_2O_3 .

12. Bismuth (Accurate Analysis).—Decompose the ore with nitric acid and evaporate nearly to dryness. The sample of .5 to 1 gram is then treated with about 5 c.c. of hydrochloric acid and heated until the solution clears. Then add 10 to 15 c.c. of sulphuric acid, and evaporate to fumes of sulphur trioxide. Filter out the lead sulphate, treat the solution with hydrogen sulphide gas to saturation, filter and extract the mixed sulphides with yellow potassium sulphide, or ammonium sulphide. Bismuth is rather soluble in sodium sulphide, alone. As copper sulphide is generally present, wash the mass back into the beaker, and warm for some time with 3 to 4 grams of potassium cyanide. Cadmium sulphide and a trace of lead will remain with the bismuth. Dissolve in nitric acid (1:2), filter, wash well, dilute to 250 to 300 c.c., neutralize the boiling liquid with ammonia (1:2), until the last drops make the solution faintly cloudy. Then add 1 c.c. of dilute hydrochloric acid (1:3), and keep hot for about an hour. Filter on a weighed filter, or asbestos felt, dry at 100°C ., and weigh as the basic chloride, BiOCl , containing 80.17 per cent of bismuth. The basic salt may be also redissolved, if preferred, then precipitated as carbonate, and finally ignited to oxide.

BARIUM

13. Barium, as obtained in the “determination of insoluble residue,” or silica, and ferrous oxide (Chapter V), remains insoluble after the silica is driven off with excess of hydrofluoric and sulphuric acids. When an insoluble residue is obtained from a leady ore, the first insoluble residues should be boiled with water containing 5 grams of ammonium chloride. Then fuse the weighed residue as described in the method for “insoluble matter

in barium sulphate ores" (1, Chapter V), and obtain the barium in the form of pure sulphate for weighing.

CADMIUM

14. Cadmium is a rare constituent of regular copper ores, and its determination would only be required in heavy zinc ores. One gram of such material may be decomposed with acids until the metals are dissolved. Evaporate the liquid with 10 c.c. of (1:1) sulphuric acid, until strong fumes of sulphur trioxide are evolved. Cool, dilute to 50 c.c., filter off the lead sulphate, if much is present and wash with a very little dilute sulphuric acid (1:20). Filtration is not, however, necessary at this stage, if the heavy metals are to be removed from the solution by reduction with aluminum. Such a reduction may carry down a part of the cadmium, which must be recovered by dissolving the precipitated metals and repeating the reduction. To separate the iron, zinc, and cadmium, proceed according to "Breyer's method for zinc." (18*a*, Chapter VII.) The heavy metals may also be precipitated as sulphides from hot (1:5) sulphuric acid, or the copper may be removed as thiocyanate (3, Chapter IV).

If preferred, the purified cadmium sulphide may finally be dissolved and titrated like zinc, standardizing the potassium ferrocyanide with pure cadmium. The cadmium may also be precipitated as phosphate according to the conditions prescribed in 21, Chapter XIV for "zinc in standard brass." Factor: $\text{Cd}_2\text{P}_2\text{O}_7 \times .56358 = \text{weight of cadmium}$.

15. Chromium in chromite or furnace refractories may be accurately estimated by the volumetric method of A. G. McKenna.¹ It is necessary to grind the material in an agate mortar (after coarse crushing) to pass a sieve of 100 meshes to the linear inch (or 40 per cm).

Fuse .5 gram of the powder with sodium peroxide in a nickel crucible for one minute, or until decomposed. The mass is extracted with water, filtered into a 500 c.c. flask and the filtrate boiled ten minutes to destroy the peroxide. Acidify the cool solution with a large excess of dilute (1:4) sulphuric acid, transfer to a liter beaker and dilute to 800 c.c. with cold

¹ *Proc. Eng. Soc. W. Pa.*, **16**, 119 — *Methods of Iron Analysis*, Phillips, 156.

water. To this solution add 100 c.c. of ammonium ferrous sulphate solution (equivalent to 7 grams of metallic iron per liter). This will reduce chromate equivalent to .3176 gram of chromium sesquioxide. The excess of ferrous sulphate may then be titrated with potassium permanganate (3.692 grams per liter), although solution 41 and 42 of Chapter III may be used equally well. For continuous work the two are made of equal value in chromium — $3 \text{ Fe} = \text{Cr}$, or 167.52 grams Fe reduce 52.0 grams Cr.

The iron in the insoluble residue may be determined by titration, as in the analysis of refractories, 23, Chapter VII.

For the complete analysis of chrome ores refer also to method 23 of the next chapter.

16. Cobalt is included with nickel, methods 1-3, Chapter VII, in order to avoid duplication.

FLUORINE

17. Fluorine is known to exist in ores chiefly in the form of calcium fluoride, and some metallurgists contend that it is of no value as an active base. Accordingly a reliable method for its estimation is included. It can be roughly determined by the process recommended by A. H. Low for such material. In carbonates (fluxes), this is a simple problem. The carbonates are boiled in strong acetic acid, after fine grinding. Then add some dilute acid and the calcium fluoride with silicates will remain insoluble. For an accurate estimation, however, proceed according to Kneeland's method in the following paragraphs.¹

Fuse .5 to 1 gram of ore, or slag (according to the percentage of fluorine), in a porcelain crucible, with 10 times its weight of a mixture of equal parts of sodium and potassium carbonates. When the whole mass has come to a quiet fusion, raise the heat to a bright red, and pour into an iron mold, saving the crucible. Cool, break up the crucible into small pieces, and transfer with the fused mass to a 15 cm. casserole (agate ware preferred to avoid bumping). Add 200 c.c. of water, and digest for one hour at a temperature near boiling, breaking up the fused lumps with a thick glass rod. If any lumps are still noticed, remove them with pincers, grind them in an agate mortar, and wash the

¹ *Modification of Berzelius' Method* — *Berichte* 21 (1888) 2843. Notes — *J. Amer. Chem. Soc.* **37** (1915) 258.

mass back into the casserole with hot water. Now boil for 10 minutes, and filter through a loose paper into a liter beaker. Wash first with hot water, then with a hot solution of ammonium carbonate, discarding the residue. Add to the filtrate 10 grams of ammonium carbonate, boil five minutes, and allow to stand in the cold for two hours. Filter through a loose filter into an agate-ware casserole, decanting as much as possible of the fluid. Wash once, or twice, with cold water.

To eliminate final traces of silica, add 20 c.c. of an emulsion of zinc oxide in ammonium hydroxide, and boil, with the dish uncovered, until no more odor of ammonia is detected. Filter into a 750 c.c. beaker and wash with hot water. To the filtrate, add a solution of calcium chloride, stirring with a rubber-tipped rod until no more precipitate is formed. Allow to settle and filter, washing with hot water. Test the filtrate for carbonates and fluorine with a few drops of calcium chloride solution.

Now transfer the filter and precipitate to a platinum dish of suitable size. Dry first, then ignite at a red heat for 20 minutes. Cool and disintegrate the mass with hot water. Add acetic acid until the solution is clear and evaporate to dryness, being careful not to decompose the residue. Moisten again with acetic acid and evaporate until there is no more odor of the acid. Wash the mass into a 400 c.c. beaker with hot water, add more water and warm until the calcium acetate is all dissolved, and add, finally, 150 c.c. more of hot water, while stirring. Digest for a few minutes in a warm place and filter, washing first with hot water, then with hot ammonium chloride, and again with hot water.

Next, transfer filter and contents to a platinum dish, dry, and ignite. Cool, moisten with cold water, add 6 c.c. of sulphuric acid (d., 1.84), and heat for a few minutes, cool again, add 3 c.c. of hydrochloric acid, and heat for a few minutes more. Cool, dilute, and transfer the contents to a 250-c.c. beaker. Add 5 grams of ammonium chloride, boil for a few minutes, cool, and add an excess of strong ammonia. Add 2 to 3 c.c. of strongest hydrogen peroxide, boil, and filter. The lime is then all precipitated from the filtrate with ammonium oxalate and determined as calcium oxide in the usual manner by titration with permanganate of potash (1 c.c. = .005 g. CaO). $\text{CaO} \times 1.392$ gives calcium fluoride (CaF_2), and $\text{CaF}_2 \times 0.4782 = \text{fluorine}$.

In the analysis of fluor-spar, add 4 parts of silica before the first fusion.

LEAD — IN ORES AND MATTES

18. Western Assay, — Ores. — Decompose .5 gram in a casserole with 10 c.c. of nitric and 10 c.c. of sulphuric acid (diluted with 1 part of water). Heat until fumes of sulphur trioxide have been escaping for at least five minutes. It is extremely important that all nitric acid be expelled. Cool, add 50 c.c. of cold water and boil until all soluble sulphates are dissolved. Filter, wash several times with hot dilute sulphuric acid (1:10 of water), then once with hot water. All the iron must be removed from the precipitate. Spread the filter on a watch glass and wash into a beaker with hot water, followed by hot solution of ammonium acetate in sufficient quantity to dissolve all the lead sulphate. Finally, heat to boiling and titrate with standard ammonium molybdate (solution 3, Chapter III). With some ores, it may be necessary to make a preliminary digestion in hydrochloric acid before the nitric and sulphuric acids are added.

19. Lead in Tailings. — Take 5 grams and proceed as before, except that the solution of the lead sulphate in ammonium acetate should be filtered from the insoluble matter in order to give a clear solution for titration. This scheme will not give a very exact assay of small amounts of lead, but will always show the presence of lead, which may be estimated with fair accuracy, by the cloudiness produced.

The method above described is reliable in presence of the elements usually present, except barium and strontium. In this case, proceed as before until the lead sulphate and insoluble matter is on the filter; then dissolve it by boiling in a mixture of 50 c.c. of water, .5 c.c. of hydrochloric acid, and 10 grams of crystallized ammonium chloride. From the solution, precipitate the lead with a strip of aluminum; wash the deposit thoroughly, dissolve it in dilute nitric acid, and proceed as in the standardization of the molybdate (solution 3), by lead foil. (See Chapter III.)

20. Lead by Electrolysis. — The original description of F. G. Hawley¹ is modified as follows: Digest .8643 gram of ore in a tall 300 c.c. beaker with 15 c.c. of chlorate mixture and evapo-

¹ *Eng. & Min. Jour.* (1910) 648.

rate to fumes of sulphur trioxide. The acid mixture is composed of 1 part sulphuric acid, 2 parts of nitric acid, and 1 part of a saturated solution of potassium chlorate in nitric acid.

Cool, add 25 c.c. of water, and bring to a boil to insure perfect solution of soluble matter. Now set the beaker in an inclined position in a funnel so that the lead sulphate may collect in one place. Cool again and decant with care through an S. & S. 597 filter, keeping the lead, as far as possible, in the beaker. Wash once with a very little water, allow to settle, decant again, and wash the filter once with a little cold water. Place the beaker under the funnel, and wash the filter with 40 c.c. of a boiling mixture of the following formula (20 c.c. nitric acid, 15 c.c. of saturated ammonium nitrate, and 5 c.c. of water). Boil to ensure complete solution of the lead, rinse into a small 90-c.c. electrolytic beaker, and electrolyze the hot solution for two hours with a current of 1.5 to 2 amperes (at a temperature of about 70° C.). Wash the anode deposit with hot water, then with alcohol, dry over a hot plate, and weigh. According to Hawley, the factor .855 then gives the percentage of lead in the deposit, and the weight of lead peroxide gives by inspection the percentage of lead. Prof. E. F. Smith has proved, however, that the factor .8643 is more uniformly correct for the lead in the peroxide, provided that the anode deposit is dried 20 minutes, or more, in a hot-air oven at 210 to 230° C. The author recommends this procedure.

Some operators prefer to dissolve the lead sulphate with warm saturated ammonium carbonate and excess of ammonia, then mix suddenly with the proper amount of nitric acid. Dr. Toisten uses ammonium tartrate, in which case the lead may be precipitated as metal (10, Chapter XIII).

21. Rapid Electrolysis.—In the absence of antimony, bismuth, molybdenum, or tellurium, the assays, already described, may be shortened, and may also become an accurate process for the estimation of traces of lead which cannot be accurately determined as the sulphate. Treat the factor weight of ore (.8643 g.) in a tall 90 c.c. beaker with 10 c.c. of nitric acid. When decomposed, add 15 c.c. of nitric acid, fill with hot water, and electrolyze the nearly boiling solution, as before; employing the Frary solenoid, if desired, and increasing the

current to 3 or 5 amperes. Time of electrolysis, 15 to 20 minutes.

Copper in solution has a good influence on the deposition of lead. If copper or similar metals are absent, it is necessary to increase the volume of the nitric acid in the hot solution to about 30 per cent. It is sometimes an advantage to interrupt the current for a minute, during electrolysis, to allow any trace of lead to dissolve from the cathode. Bismuth and tin tend to come down with the lead, if appreciable amounts are present, but may be removed after the deposit is weighed.

22. Chromate Method for Calcareous Ores. — H. A. Guess¹ devised a process for low-grade, limy material which is not readily tested by the molybdate method. The *standard solutions* are: potassium chromate, 100 grams per liter (solution 36, Chapter III); sodium thiosulphate solution containing either 18 or 36 grams per liter. Solution 50, Chapter III, adopted for the iodide titration of copper, may also be used for lead, if standardized against pure lead.

Analysis. — To an ore-charge of 1 to 5 grams in a broad 250 c.c. beaker, add 3 to 5 c.c. of strong nitric acid, 15 c.c. of hydrochloric acid, and digest until all soluble matter is dissolved and the excess of acid is reduced to about 8 c.c. The time required is 15 minutes. Remove the flask and add a slight excess of dilute ammonia. Eighty per cent acetic acid is then added slowly with vigorous shaking until the smell indicates a decided excess. Follow with 5 c.c. of concentrated ammonium acetate to insure the solution of any other lead salts. In absence of antimony or gelatinous silica, add to the hot undiluted and unfiltered solution, an excess of about 10 c.c. of a 10 per cent solution of potassium chromate, the total volume being less than 50 c.c. After shaking and settling about five minutes, the contents are to be filtered through a close filter.

If these directions are followed, the result will be a granular precipitate. Wash this lead salt several times with hot water containing .5 per cent acetic acid, omitting the latter acid, however, if the ores are low in iron, or manganese, and if the main solution was strongly acidified. Set the funnel over the beaker and pass hot hydrochloric acid (1:1) through it until the lead is dissolved, then wash the filter until free from chromate. Add

¹ *Trans. A. I. M. E.* **35**, 367.

.5 to 2 grams of potassium iodide, and titrate directly with the standard thiosulphate; of which 1 c.c. equals 5 mg. of lead. By having about 50 c.c. of (1:1) hydrochloric acid in 200 c.c. of the warm solution, any tendency to the formation of lead iodide is completely checked, and the end reaction is just as sharp as in a second method devised for richer ores.

MANGANESE

23. In Slags. — Manganese is usually determined, in the western States, by titrating the neutral solution of the sulphate (according to Volhard), with potassium permanganate. Dissolve .5 gram of slag exactly as for iron (6 and 7, Chapter V), but use less hydrochloric acid. Add about 5 c.c. of nitric acid and boil until most of the chlorine is expelled. All Lake Superior cupola slags are dissolved as in 7 just quoted, using a beaker 5.5 cm. in diameter and 12.5 cm. in height, which is filled with boiling water before neutralization, within one-half inch of the top. Add a weighed excess (5 to 25 grams) of fine dry zinc oxide with rapid stirring, as in the analysis of steel. If a blank test of 25 grams of reagent requires more than .50 c.c. of the permanganate, the zinc oxide is not sufficiently pure for the purpose. For Western slags, dilute with hot water to 100 c.c. and add the emulsion of zinc oxide, or the powder, until the iron is completely precipitated. Boil for two minutes and titrate while hot, in the presence of the precipitate, with potassium permanganate. On standing a few seconds after stirring, the mass quickly settles, and the pink color at the end-point can be easily detected in the supernatant liquid. The standard solution, used for lime, may also be taken for this titration; $0.5878 \times$ its calcium oxide value giving the value of the solution in manganese, Mn. The titer in metallic iron may be multiplied by .2951 if desired. To make a test of the zinc oxide, fill a beaker with hot water, add 1 c.c. of sulphuric acid, stir in the requisite weight of zinc oxide used in regular work, and titrate as usual.

24. Manganese in Rich Ores. — According to A. A. Blair, we may take enough rich material to contain .05 gram of manganese, when using .1 normal permanganate. Fuse 1 gram of such ore in a large platinum crucible with 10 grams of potassium bisulphate, 1 gram of sodium sulphite, and .5 gram of sodium

fluoride. The heating should be slow until effervescence ceases. After complete fusion, cool the product, heat carefully with 10 c.c. of sulphuric acid (1.84), then cool, dissolve in water and make up to a definite volume, from which, after mixing in a dry beaker, an aliquot portion may be titrated. The slight amount of barium sulphate has no influence.

NOTE. — For the determination of *manganese* as phosphate, refer to the analysis of brass, 16, Chapter XIV.

25. Manganese by "Sodium Bismuthate." — This simple titration process is capable of great accuracy, particularly with iron, steel, and rich ferruginous ores. Originally devised by Schneider,¹ it has been developed by Reddrop & Ramage, Brearley and Ibbotsen in England and improved by Blair,² Brinton,³ Blum,⁴ and the Society for Testing Materials in the United States.

Titration with Permanganate. — .015 to .02 gram of manganese may be conveniently titrated with .03 normal reagent. Rich ores are titrated with .1 normal permanganate (3.1 grams of salt per liter).

The reagents employed in standardization of permanganate are: *First*, nitric acid diluted by mixing 500 c.c. of acid (d., 1.42) and 1500 c.c. distilled water. Acid for washing — a 3 per cent solution by volume. *Second*, potassium permanganate for titration, 41, Chapter III. *Third*, a solution of 12.4 grams of crystallized ferrous ammonium sulphate and 50 c.c. (of a mixture of equal volumes of concentrated sulphuric and phosphoric acids) diluted to one liter. For .1 normal permanganate, 39.2 grams of the double salt, or 27.8 grams of crystallized ferrous sulphate, and 50 c.c. each of sulphuric and phosphoric acids are diluted to a liter. Test the iron solution every day against the permanganate. If the reagent is slightly aged at first, it will remain practically unaltered for months. The same conditions should prevail in the standardization and analysis.

Standardization. — Measure into a 200 c.c. flask 50 c.c. of the (1 : 3) nitric acid, cool in ice water to less than 5° C., add a very

¹ *Dingler Polytech. J.* **269**, 224.

² *J. Am. Chem. Soc.* **26**, 793. ³ *J. Ind. and Eng. Chem.* **3**, 237.

⁴ *Eighth Inter. Congress of Chem.*, **1**, 62.

little sodium bismuthate, dilute with 50 c.c. of the 3 per cent acid, filter through an asbestos felt into a 300 c.c. flask, wash with 50 c.c. of the 3 per cent acid, and titrate at once, after the addition of 25 c.c. ferrous sulphate solution. If the felt is well coated with bismuthate, it is unnecessary to add any to flask. This gives the value of the ferrous sulphate.

The *permanganate* may be valued: *First*, by multiplying the iron value by .4919. *Second*, by the use of a solution of pure manganous sulphate, in which the manganese is determined by evaporating a portion and heating for 4 hours at 450 to 500° C., then multiplying the weight by .3638. Oxidize and titrate 1 to 3 grams of this solution, which contains 5.749 grams of anhydrous sulphate in 1000 grams. Or 4.124 grams may be made up to 500 grams with distilled water and 1 gram will contain .003 gram manganese. A color is given to 50 c.c. of liquid by .00005 gram of manganese. Every trace of nitrous acid must be previously boiled out and the titration completed within ten to fifteen minutes after filtration. The solution changes in fifteen minutes at 40° C., but will remain unaltered several hours at 5° C. A large excess of bismuthate, over .5 to 1 gram, is inadvisable.

Third method for valuation of permanganate, — comparison with manganese in a standard steel or ore. *Fourth*, by specially purified (reagent) sodium oxalate, which has been well dried in an air oven at 100 to 105° C. before use and preserved in a small glass stoppered bottle. Dilute the oxalate solution to 75 c.c. for .03 normal permanganate and 250 c.c. for the .1 normal reagent. The initial temperature should be 80 to 90° C. and the final 60° or higher. This is the best method if strictly correct oxalate is at hand. Such a correct salt may be obtained from the U. S. Bureau of Standards. The value of the permanganate in terms of the oxalate is then to be multiplied by .16397 to obtain the equivalent in manganese. The stronger permanganate may also be used to test the sodium arsenite used in the second alternative method of titration of steels and ores.¹

Titration by Sodium Arsenite. — Make up a *stock solution* by heating in a flask on the water bath 15 grams of arsenious oxide (As_2O_3) 45 grams of sodium carbonate and 150 c.c. dis-

¹ *American Society for Testing Materials. Official Method for Steel in Year Book, 1914, 177.*

tilled water. Cool the solution and make up to 1000 c.c. with distilled water. A *standard solution* is made by diluting 300 c.c. of the "stock solution" to one liter and titrating against the 1. normal permanganate which has been standardized by the fourth method above given. The solution may be adjusted so that 1 c.c. is equivalent to .1 per cent of manganese when a one-gram sample is taken;—formula 47, Chapter III.

Analysis of Ores and Slags.—If the ore dissolves rather easily, treat 1 gram with 12 c.c. of hydrochloric acid (d., 1.2) in a 120 c.c. Erlenmeyer flask, evaporate almost to pastiness, and then add 4 c.c. of sulphuric acid (d., 1.84). By boiling down to fumes over a free flame with the flask in a holder, the hydrochloric acid is so completely expelled that no cloud test can be obtained with silver nitrate. This is very essential. Take up the residue with 50 c.c. of the (1:3) nitric acid, cool at least to 15° C., but to 5° C. for accurate work. Then add an excess—.5 to 1 gram of sodium bismuthate and agitate for three to four minutes. Pour in 50 c.c. of the cold 3 per cent nitric acid (as in standardization) and filter through an alundum crucible or asbestos felt. Wash with about 50 c.c. of 3 per cent acid. Titrate at once by potassium permanganate after addition of 25 c.c. ferrous sulphate solution, or directly with the sodium arsenite if preferred.

A few ores will not yield all the manganese to this treatment. If the residue is dark, it should be filtered off and fused with a very small amount of potassium bisulphate. Metzger and McCrackan claim good results by treating the sample with as much as 10 to 15 c.c. of sulphuric acid. They add subsequently 1 to 2 grams of the sodium bismuthate after the hydrochloric acid has been removed, and boil the solution twenty minutes to oxidize the manganese. Filter and wash with about 50 c.c. of the 3 per cent nitric acid as before.

MOLYBDENUM AND OTHER RARE METALS

26. In copper refineries, tests are seldom required for any of the rarer metals except selenium, tellurium, gold or platinum in copper or ores, and occasionally platinum or palladium in electrolytic slimes. For the assay of the precious metals, consult 9, 10, Chapter VIII.

The determination of selenium and tellurium is taken up in

10, Chapter VII and again in the analysis of metallic copper, 17, Chapter XIII.

The latest methods for the identification of tungsten, vanadium, and other rare metals are summarized in the "Report on Rare Metals to the Committee on Analysis,"—8th International Congress of Applied Chemistry (1913), pp. 1 to 24.

CHAPTER VII

SPECIAL DETERMINATIONS IN ORES, SLAGS, AND MATTE — CONCLUDED

FURNACE REFRACTORIES

NICKEL AND COBALT

1. Titration of Nickel in Matte. — For nickeliferous matte, one may use a rapid method for the titration of nickel (and copper) which involves the prior separation of the copper as sulphide, and its subsequent titration in the usual way by potassium iodide, as in Chapter IV. The nickel is titrated in alkaline sodium citrate solution with potassium cyanide. This rapid assay is practiced by the Canadian Copper Company.

To prepare for titration, weigh .5 gram of matte into a 200 to 300 c.c. lipless beaker. Add 15 c.c. of strong hydrochloric acid, cover, and set the beaker on the hot plate. The solution will be complete in 3 to 5 minutes. When the matte is all dissolved, add a single drop of nitric acid, and boil for a few moments. Dilute the solution to about 100 c.c. with hot water and pass hydrogen sulphide gas until the precipitation of the copper group is complete. Filter rapidly through a 597 S. & S. filter, receiving the filtrate into a 500 c.c. griffin-form, Jena beaker. Wash five to seven times with hot water, and set the filtrate on a hot plate to boil. Spread out the filter of copper sulphide against the side of the beaker, keeping that part of the paper holding most of the precipitate, below the rim of the beaker. Wash the paper as free as possible from the sulphide, using as little hot water as possible. Now add 3 to 4 c.c. of strong nitric acid and place the beaker to heat. Remove any adhering copper from the paper, or rod, by saturated bromine water.

Evaporate the copper solution over a free flame, almost, but not quite, to dryness. The yellow globule of sulphur should not show any dark color. Wash down the sides of the beaker, using, however, no more than 5 c.c. of water. Add, drop by

drop, a strong solution of sodium carbonate just in sufficient amount to form a slight permanent precipitate. Redissolve this in dilute acetic acid, using a slight excess, keeping the volume less than 10 c.c. Titrate as in method 1, Chapter IV, with sodium thiosulphate (50, Chapter III) adding six times as much potassium iodide (formula 38) as there is copper present.

Nickel. — The nickel solution is treated while the copper is being prepared for titration. The nickel solution should be boiled for 2 to 3 minutes to expel the hydrogen sulphide remaining from the copper precipitation. While still boiling, and after expulsion of the hydrogen sulphide, add about 1 gram of potassium chlorate and boil for one half minute. If the chlorate has been added before all the gas is expelled, sulphur will separate and it is very difficult to obtain a clear solution. However, prolonged boiling with the addition of more potassium chlorate will usually clear the solution. Cool slightly and add 20 c.c. of sodium citrate solution (47, — 200 grams per liter). Neutralize with ammonia, using a distinct excess. Cool in running water. When the solution is quite cold, adjust the alkalinity by adding cold dilute hydrochloric acid, or ammonia, as required. The correct degree of alkalinity is a distinct but *small* excess of ammonia.

The liquid is now titrated for nickel by a modification of the method of T. Moore. Add 5 c.c. of potassium iodide solution and 5 c.c. of a solution of silver nitrate (1 gram per liter). If a permanent cloudiness forms after the addition of the potassium iodide and before the addition of silver nitrate, more ammonia must be added until the solution becomes quite clear again. Then add the silver nitrate, which will cause a permanent cloudiness. Run in potassium cyanide with constant stirring till the solution is almost clear again. Now allow to stand while titrating the copper, as already described. Before that operation is completed, the nickel will have become cloudy again. Carefully add more potassium cyanide till the nickel solution becomes quite clear. These standard solutions are standardized against matte which has been analyzed by exact electrolytic methods.

NOTE.—The potassium cyanide solution contains 24.5 grams of 98 per cent salt per liter (formula 31, Chapter III). For very accurate work, the amount of potassium cyanide required

to dissolve the precipitate of silver iodide should be deducted from the total number of cubic centimeters required to clear the solution. (This usually amounts to about .15 c.c.)

For high grade and "Bessemer" mattes, the procedure is the same except that 40 c.c. of hydrochloric acid are required in dissolving the matte. Five c.c. of the sodium citrate is sufficient. With the Bessemer mattes, the potassium cyanide must be run in very rapidly until near the end-point, otherwise nickel cyanide may form. This is difficult to dissolve and the end-point may be passed. (Zinc uses up cyanide. Small amounts of cobalt do not interfere, but larger amounts spoil the titration.)

2. Nickel with Cobalt by Electrolysis.— If copper is not to be determined, an ore may be treated in a lipped beaker with a mixture of acids and evaporated to strong fumes of sulphuric anhydride. Some ores, or mattes, may be decomposed very easily by digestion with sulphuric acid and potassium bisulphate, in the same manner as for arsenic.

The copper, etc., may then be precipitated from the diluted solution by hydrogen sulphide and the remaining gas boiled out of the filtered solution. A more rapid and satisfactory separation, however, is that by rapid electrolysis, placing the beaker in a Frary rotary apparatus. The solutions are subjected to 4 to 4.5 amperes at 2.75 volts electrode tension when a five gram sample is tested, or 3 amperes for a one-gram sample.

Conducted through a rheostat, or lamp resistance, the current from a 110-volt circuit will deposit 5 grams of copper in 2.5 hours.

When the iron percentage is low, the best electrolyte contains about 6 to 7 c.c. of nitric acid and 10 c.c. of sulphuric acid.

When the iron is over 10 per cent, an excess of nitric acid may retard deposition. If any manganese is present, it may be removed with the iron, or after it, by boiling the faintly ammoniacal solution with an excess of bromine or ammonium persulphate. If a separate assay for zinc is required, that element may be first removed by rendering the solution faintly acid with acetic acid, adding a quantity of glacial acetic equal to one-fifth of the volume of the solution, and saturating the cold solution thoroughly with hydrogen sulphide. If preferred, the Waring method of precipitation in formic acid solution may be conducted

as described under "zinc." The white sulphide may be colored with a trace of lead or copper sulphide. The zinc is filtered out and washed with hydrogen sulphide water containing a little ammonium acetate, after which the hydrogen sulphide is boiled out of the filtrate. The solution can now be electrolyzed, although a little better result may be obtained by adding 5 c.c. sulphuric acid and boiling down to fumes to remove most of the acetic and any nitric acid present. Neutralize the solution with ammonia (d., .9) and add 30 c.c. excess. The total volume may be 100 to 200 c.c., according to the amount of cobalt and nickel present.

If the Frary solenoid is used (Chapter I), the strength of current may be 3 to 4 amperes, with an electrode tension of 2.5 volts, and the time about one and a half hours, or less. The solution must not become acid during the deposition. The end-point is tested by withdrawing 1 c.c. and testing with hydrogen sulphide. The current for deposition by the slow method is .5 amperes per sq. dm. at 2.5 volts potential. Two accurate methods for preliminary separation of cobalt and nickel are given later. The cobalt and nickel are then electrolyzed separately. The cathode deposits must always be tested for a trace of iron, and occasionally platinum or copper.

3. Ether Method for Cobalt, Nickel, and Zinc. — This separation was devised by H. Koch primarily for Mansfeld ores. The separation of the large quantity (about 25 per cent) of iron was formerly made by the "basic acetate." Of late, the well-known "ether method" of Rothe is used to advantage. The shaking apparatus of the inventor is not used. The same purpose is accomplished by a simple shaking cylinder and a removable flask adjoining, as shown in Fig. 12.

A 5-gram sample of powdered crude ore in a 16 cm. evaporating dish is moistened with water to avoid adhesion of the fines to the dish, which would occur if the dry substance were heated with acid. After decomposing with acid, the liquid is evaporated to dryness several times on the water bath with hydrochloric acid to convert the nitrates to chlorides, and the separated sulphur is burnt out by heating on a small sand bath. The cooled residue is treated again with hydrochloric acid, evaporated, and taken up with 12 to 15 cm. of water.

This concentration must be adhered to, since with greater

dilution the later separation of ferric chloride is incomplete. The solution is washed into the shaking cylinder by means of 40 c.c. of hydrochloric acid (1:2), with 50 c.c. ether added, and strongly shaken. After the subsidence of the copper chloride solution, the ethereal extract is drawn off by the bottle syphon, a second equal quantity of ether added, and the shaking repeated. A third similar extraction is sufficient to remove the last trace of iron. (This operation may be hastened by making one ammonia precipitation of the iron, followed by one ether separation only.) The liquid remaining in the shaker is transferred to a 750 c.c. lipped beaker, to precipitate the copper and arsenic with hydrogen sulphide. For safety, it is recommended to shake out the ether extract twice with some hydrochloric acid to recover a trace of nickel as chloride, which will then be added to the main portion in the beaker.

After filtration, the sulphides are evaporated to dryness with nitric and sulphuric acids, taken up with water, the separated lead sulphate filtered off, and washed with dilute sulphuric acid. In the filtrate, manganese and the small trace of remaining iron are precipitated with ammonia (and bromine water). Repeated precipitation and solution of the latter in hot sulphuric acid with the addition of a few drops of solution of sulphur dioxide is found necessary, as otherwise cobalt remains in the manganese. The liquid is then neutralized with dilute sulphuric acid until the last drop renders it slightly acid (to methyl orange indicator), and the zinc is precipitated with hydrogen sulphide. After standing twelve hours, the sulphide is filtered off with the aid of the hydrogen sulphide water, to which some ammonium

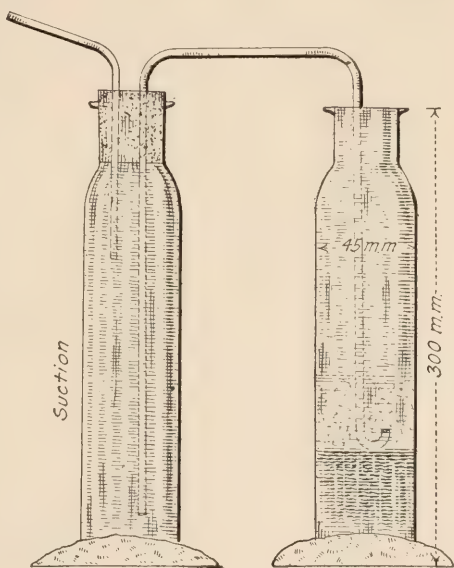


Fig. 12.—Cylinders for Ether Method.

sulphate has been added, and the filtrate is concentrated on the water bath to destroy the hydrogen sulphide. The solution must first be acidified with sulphuric acid, since nickel sulphide might separate from it if nearly neutral. The concentrated liquid is then poured into a 1.5-liter beaker, saturated with ammonia, and electrolyzed for the precipitation of cobalt and nickel.

4. Separation of Cobalt from Nickel.—Precipitation with potassium nitrite is rather uncertain, and two more delicate separations are now preferred. The first scheme is adapted to the separation of a *little cobalt from much nickel*. This is accomplished by the use of nitroso- β -naphthol, $C_{10}H_6(NO)$; a method due to Knorre and Illinski.¹

Remove the heavy metals from solution, either by hydrogen sulphide or by electrolysis, then take out the iron and alumina and follow with a second separation by ammonia. A very large amount of iron, with little alumina, may be separated by Koch's ether method, but if the cobalt, nickel, and zinc are only traces, as in pure ores and high grade metal, two precipitations with ammonia are sufficient. (See Waring's method for zinc.) If manganese is present, this is removed by bromine or ammonium persulphate. To the nearly neutral solution of the sulphates of cobalt, nickel, and zinc (or the solution of the cathode deposit of combined elements), add 4 to 5 c.c. strong hydrochloric acid, warm, and add a hot saturated solution of the naphthol reagent in 50 per cent acetic acid, as long as precipitation continues. Allow to settle for a few hours at room temperature, wash first with warm 12 per cent hydrochloric acid until all the nickel is removed, then wash with water to remove the acid. The precipitate can be ignited with oxalic acid in a Rose crucible, finally reducing in hydrogen. The best way, however, is to dissolve in a little nitric acid and 3 to 5 c.c. sulphuric acid, and evaporate to fumes. Then dilute, neutralize with ammonia, add 30 c.c. in excess, and electrolyze with a platinum cathode.

The data for the method are: volume 30 to 150 c.c., according to the amount of cobalt; area of cathode surface 50 or 100 sq. cm.; current .1 to .5 ampere, at about 2.5 volts potential. With revolving anode or solenoid, pass 4 amperes through coil and sheet cathode; time about 1 to 1.5 hours. The final test

¹ *Ber. Deutsch. Chem. Gesell* (1885), 699.

is made with hydrogen sulphide water. Test the deposits for purity.

5. Separation of a little Nickel from much Cobalt or Zinc. —

The beautiful reaction of nickel with dimethyl glyoxime, discovered by Tschugaeff and Brunck,¹ is made the basis of the method. This may even be applied in presence of the iron and alumina by holding them in solution with an excess of sodium citrate, or tartaric acid (2 to 3 grams), as in the titration method already described. It is better, in this case, to add also 2 to 3 grams ammonium chloride. Prepare the solution, ordinarily, by removing the heavier metals, including iron, alumina, and manganese, by the separations already described (4). Then acidify, after boiling out all hydrogen sulphide, until the solution contains about 5 c.c. of free hydrochloric acid. The solution should be diluted so that 100 c.c. does not contain more than .1 gram of cobalt; and a standard 1 per cent or 2 per cent alcoholic solution of the glyoxime reagent is then added to the boiling solution until the amount is about five times that of the nickel and cobalt. Ammonia is then added until the solution is slightly alkaline, and the precipitate allowed to settle some time on the steam plate. The liquid is filtered hot through a pure asbestos felt which has been dried and weighed. The washed salt is dried to constant weight at 110° to 120° C. The compound has the symbol $C_8H_{14}N_4O_4Ni$, which corresponds to 20.325 per cent of nickel. A method for the recovery of the oxime is to be found in the papers quoted. The salt is almost insoluble in water and only very slightly soluble in alcohol or acetic acid.

If accurate results are desired with zinc ore and other rich products, it is necessary to dissolve the pink precipitate in hydrochloric acid (1 : 1), wash the filter, and repeat the separation with a little more of the glyoxime. The filtrates from the nickel may then be treated for the separation of zinc from the cobalt by precipitation with hydrogen sulphide in a formic, or acetic acid solution (as in 2), unless the cobalt was removed before the nickel by method 4.

Instead of weighing the nickel glyoxime, it may be dissolved in diluted nitric or hydrochloric acid, evaporated to fumes with 5 c.c. of sulphuric acid, and the sulphate neutralized with excess

¹ *J. Soc. Chem. Ind.* **24**, 941; *Zeit. Angew. Chem.* **20**, 38, 44; also abstract *J. Am. Chem. Soc.* **2**, 240.

of ammonia and electrolyzed as in 2. The accuracy required and the amounts or relative proportions of cobalt, nickel, and zinc, should influence the choice of the method of separation of these elements.

NOTE (on Zinc). — The direct *determination of zinc* in slags, or ores, is recorded in 17, near the end of this chapter.

POTASSIUM AND SODIUM

6. Potassium and Sodium (with Lithium) are estimated in silicates, such as clay, slags, or ores, by removing all other elements from the solution successively, or by sintering in a platinum crucible with an excess of calcium carbonate and ammonium chloride, extracting with hot water and precipitating any lime from the extract.

Solution Method. — Treat two grams of dried clay, or furnace product, with an excess of hydrofluoric acid and sulphuric acid in a platinum dish. In the case of slags, it is sometimes advisable to add nitric acid. Heat gently without baking until all free sulphuric acid is removed. A. H. Low recommends the direct extraction of this residue with hot ammonium hydroxide. Such treatment should be proved correct before acceptance with unknown material. Usually, the residue from slags, or ores, should be dissolved in dilute hydrochloric acid, and the ferric hydroxide and alumina removed by two successive precipitations with ammonia in a platinum dish. Filter and wash, then remove any heavy metals by hydrogen sulphide, and filter again. Evaporate to dryness in a platinum dish and volatilize nearly all the ammonium chloride. Dissolve and precipitate calcium and magnesium by boiling with a slight excess of ammonia and ammonium carbonate. Filter, evaporate filtrate, and remove salts by gentle ignition as directed in the next paragraph.

Determination as Sulphates. — After the metals and alkaline earths are separated, evaporate the filtrate or extract to dryness in a platinum dish, and heat carefully at the lowest visible red heat, or below that point, until the ammonium salts are removed. Dissolve the residue in 5 to 10 c.c. of hot water. If no separation of potassium from sodium is desired, the hot solution may be tested with a few drops of ammonium carbonate, filtered into a weighed platinum crucible, and the solution and washings evapo-

rated again to dryness on the steam plate or water bath. Ignite very gently as before and after cooling ten minutes in a desiccator, weigh the sulphates. The sulphur trioxide in combination may then be found by dissolving the residue in a very little water, adding a drop of hydrochloric acid, and precipitating with barium chloride. Allow to settle, filter, wash, ignite, weigh the barium sulphate, and calculate the sulphur trioxide. Deduct this amount from the total weight of sulphates to obtain the total weight of oxides of potassium, sodium (and lithium if present).

Determination as Chlorides. — To remove the small amount of sulphates from the purified solutions of potassium and sodium, either add barium acetate, or a slight excess of barium chloride.

In the former case, boil the solution, filter, wash out soluble matter, evaporate to dryness, and then heat to the lowest visible red to destroy the acetates. Treat the residue with a little water, filter out any insoluble barium or magnesium carbonates, add 2 to 3 drops of barium hydroxide solution, and take again to dryness. Dissolve in 5 c.c. of water in all cases, filter into a weighed crucible, concentrate to a low point, and if the liquid does not remain clear, filter into another clean, weighed crucible. Add two drops of hydrochloric acid, heat very carefully to the lowest perceptible red, cool in a desiccator for ten minutes, and weigh as chlorides of sodium, potassium, and lithium, if present. Test the purity of the residue by dissolving in 5 c.c. of water, evaporating with a few drops of ammonium carbonate, and redissolving in 5 c.c. of water.

If the liquid is not clear, filter on a very small paper, wash with a few drops of water, evaporate in a weighed crucible, ignite gently, and weigh again.

SEPARATIONS — POTASSIUM FROM SODIUM, (AND LITHIUM)

7. Potassium is separated from the sodium (or lithium) by dissolving the weighed chlorides in the least amount of warm water, and treating the clear solution in the crucible, or a No. 3a casserole, with sufficient 10 per cent solution of platinic chloride to convert all the sodium and potassium into double salts. Any unchanged sodium chloride would not dissolve in absolute alcohol. Assuming the mixture to be mostly sodium chloride, 116.92 parts of sodium chloride will require 195.2 parts of platinum, or its equivalent as chloride. A slight excess of .5 to 1 c.c. should be

present in addition to the calculated amount. Concentrate below the boiling temperature until the mass solidifies upon cooling.

Add a little absolute alcohol (according to A. H. Low, methyl is the best); stir well with a bent rod or wire, then filter through a small paper or a weighed asbestos felt. Repeat this extraction and washing with the alcohol until a pure golden yellow residue remains. Lithium, if present, is extracted with the sodium. William Crookes recommends the addition of $\frac{1}{6}$ part of ether to the alcohol. If a dry filter is used, dry the washed contents in an oven at 80 to 90° C., then transfer as much as possible to a watch glass, and wash the adhering salt with hot water into a weighed platinum crucible. Evaporate the solution at a low heat, add the rest of the precipitate, dry the whole at 160° C., and weigh the potassium platinic chloride. The percentage of potassium oxide, corresponding to the K_2PtCl_6 , may be found by multiplying by the factor .19376 (or .30673 for KCl). A. H. Low considers that the older factor of .3056 is the more correct one as slight changes occur during evaporation. The sodium chloride is taken by difference and multiplied by .53028 to obtain sodium oxide, Na_2O . Lithium may be separated as phosphate.¹

8. Indirect Separation. — This is only applicable when the sodium and potassium are present in nearly equal amounts. *First*, determine the total percentage of chlorine in the weighed chlorides of potassium and sodium by precipitation, or by titration, with silver salt. *Finally*, apply the rule of A. H. Low, which is the most simple form published. Subtract 47.56 from the percentage of chlorine in the weighed chlorides of potassium and sodium. Divide the remainder by 13.098 and the result will be the per cent of sodium chloride in the mixture of the two chlorides. This assumes that the lithium is negligible.

The chloride of ammonium, which so often causes trouble by creeping during evaporation, may be decomposed very easily by adopting a suggestion of J. L. Smith. Evaporate the solution (after removal of the lime and magnesium salts) to a low point, transfer to a flask or tall beaker with a very little water, add 3 to 4 c.c. of hydrochloric acid for every gram of ammonium chloride present, and heat at a temperature a little below 100° C. until action ceases. Transfer to a small porcelain casserole,

¹ Hillebrand, *Bull.* 422, *U. S. Geol. Survey*. (Fresenius, *Quant. Anal.*)

evaporate with hydrochloric acid to dryness, treat again with a little ammonium carbonate, preceded by barium acetate, as already described, and then filter back into the weighed platinum dish, or crucible.

9. Potassium and Sodium (by the sintering method of J. Lawrence Smith ¹). — The alkaline metals in nearly all silicates, except possibly spinel, or some of the silicates of heavy metals, may be converted into soluble chlorides by slow sintering in a platinum crucible with an intimate mixture of pure ammonium chloride and calcium carbonate. The alkalis are then leached out with hot water.

Triturate 1 gram of the sample (in the form of impalpable powder) with 1 gram of pure ammonium chloride in an agate mortar, then mix with 8 grams of calcium carbonate, transfer to a large platinum crucible, and cover tightly. Heat in a slightly inclined position with a very small flame at a heat which will gradually drive off ammonia gas but not ammonium chloride. When the ammonia is removed (which should require fifteen to twenty minutes), raise the temperature so that the lower half or three-fourths of the crucible are maintained for one hour at a dull red heat. Transfer the cooled mass to a large platinum dish with 100 c.c. of hot water, boil, and break up any large particles with a small pestle. Filter and wash with hot distilled water, boiling the residue with more hot water. Test this washed residue with excess of hydrochloric acid to prove that the clay, or furnace product, was all decomposed.

To the filtrate, add 1.5 grams of dry chemically pure ammonium carbonate, evaporate carefully to 40 c.c., add a little more carbonate and a few cubic centimeters of ammonia, and filter through a small paper. Wash the filter with a little water, and then proceed to remove the last traces of calcium and magnesium by evaporation, gentle ignition, and repeated treatment with ammonium hydroxide and carbonate. No addition of barium salt is necessary, if no sulphates are present. The chlorides are separated as in the former method (7).

SELENIUM AND TELLURIUM IN SLAGS OR ORES

10. Selenium and Tellurium are separated from large quantities of iron salts, and from some heavy metals, by precipi-

¹ *Am. J. of Sci. and Art*, 3d series, **1**, 269.

tation with sulphur dioxide in acid solution. The metals are redissolved, when a separation of the two is required, and separated from each other by fractional precipitation from a hydrochloric acid solution by means of sulphur dioxide. The amount of sample to be taken (5 to 25 grams) depends on the amount of the rare elements judged to be present in the material tested.

Ores and Slags. — Digest in a mixture of strong nitric and sulphuric acids treating the insoluble residue with hydrofluoric acid, if necessary to complete decomposition. Evaporate on the water bath with a slight excess of sulphuric acid until the other acids are practically removed. In the absence of copper or similar metals a known amount of ammonium nitrate, potassium nitrate, or zinc nitrate should be added before evaporation, sufficient to form double salts with the selenium and tellurium and prevent any loss of those elements. Redissolve the salts in water and filter out any lead sulphate, etc. At this point there should be no hydrochloric acid, whatever, in the solution. Selenium and tellurium may now be separated completely from iron and copper, or other metals, with the exception of gold, by heating to 85 to 90° C. and saturating the liquid with sulphur dioxide (prepared according to Chapter III).

Keep hot for one hour, or long enough to remove any yellowish color in the solution; finally cool the liquid while the gas current is passing and allow to settle over night. Filter on a pure asbestos felt, made from acid-washed, ignited material, wash with dilute acid, then with water, dry at 100 to 105° C., and weigh. If accurate results are desired, ignite the felt before use, cool, and weigh; then moisten with water, dry in the oven at 100 to 105° C., and weigh again. This weight may be .5 to 1 mg. heavier than the first. After drying and weighing the dried precipitate, ignite to redness, and obtain the elements by loss as a check, using the first ignited weight of the felts for comparison.

In this, or the following method of separation, the filtrates from the precipitation of either selenium or tellurium should be charged a second time in the same way with sulphur dioxide and allowed to settle, then filtered through a second weighed filter, if a trace of precipitate appears.

Separation. — If selenium and tellurium are to be separated, the first felt need not be weighed. The reduced metals are

filtered off, then redissolved in a very little strong nitric acid, the asbestos filtered out, and the solution evaporated to dryness on the water bath with the addition of an amount of ammonium or potassium nitrate sufficient to combine with the metals. If five drops of sulphuric acid are also added to convert the salts to sulphates, the subsequent reduction takes place quickly. Dissolve the salts in 90 c.c. of hydrochloric (d., 1.2) and 10 c.c. of water, heat nearly to boiling for one minute to reduce any nitrates and convert the selenium to a lower chloride. Saturate the solution with sulphur dioxide, passing the gas until the solution is cold. Settle as before, filter, wash with 90 per cent hydrochloric acid, dry, and weigh as directed for the estimation of the two elements together. The washing is completed with water to dissolve any sodium chloride, but this wash water should not be allowed to dilute the filtrate until a second test has been made with sulphur dioxide to insure the complete separation of the selenium. To determine the tellurium in the total filtrate, dilute it with four volumes of water, charge again with sulphur dioxide, and proceed exactly as directed for selenium, finally igniting the dried felt as a check on the weight by drying.

The main solution of the original sample may be taken for the estimation of arsenic and antimony by usual methods. See also Chapter XIII.

11. The second method for selenium and tellurium (that of Edward Keller) depends on the preliminary separation of the rare elements from the copper by repeated precipitation with ammonia and excess of ferric salts. The iron oxide should be at least twenty times the weight of the selenium and tellurium. Ammonium ferric sulphate is added if necessary, to obtain the requisite amount. The copper should be completely removed by repeated precipitation and filtration, or copper selenide will be formed in the subsequent treatment. *This compound is insoluble in sodium sulphide.* Finally dissolve the iron hydroxides in (1 : 3) hydrochloric acid, dilute to 400 c.c., and precipitate the selenium, etc., in the cold by hydrogen sulphide. Filter, extract by repeated treatment with cold, then hot, dilute sodium sulphide solution, and evaporate the extract to dryness on the water bath. Decompose the sulphur with fuming nitric acid, or with hydrochloric acid and potassium chlorate.

Evaporate to dryness again on the water bath, then proceed as in the previous method for the precipitation of the selenium in strong hydrochloric acid solution by means of sulphur dioxide.

TIN IN ORES — BY TITRATION

12. Tin, in regular analysis, is obtained with the sulphides of arsenic and antimony (method 10, Chapter VI). A. H. Low has devised a good volumetric method, the titration of stannous chloride by iodine.

The liquid remaining in the still after distillation of arsenic may be taken. Or tin and antimony may be obtained from the filtrate remaining after the precipitation of arsenic by hydrogen sulphide in (2:1) hydrochloric acid. Dilute this filtrate with four parts of water and precipitate the tin and antimony, then filter and wash. Dissolve the sulphides in a little pure yellow ammonium sulphide, and transfer the solution to a 300 c.c. Kjehldahl flask with a long neck. Add 15 c.c. of sulphuric acid and 3 grams of potassium sulphate and boil down to fumes of sulphur trioxide. Now add .25 gram of solid tartaric acid and boil until all sulphur is expelled and most of the free acid. The antimony will then be reduced to the "ous" condition, and is ready for titration with tenth normal permanganate which has been standardized against pure antimony.

Dissolve the cooled residue in 50 c.c. of water and 10 c.c. of strong hydrochloric acid, boil out any sulphur dioxide, add 10 c.c. more of the acid, dilute to 200 c.c., cool to room temperature and titrate directly for antimony.

The tin is determined by washing the titrated solution into a 500 c.c. round-bottomed flask with 50 c.c. of strong hydrochloric acid and adding a reagent which will reduce the stannic compound to stannous chloride, ready for titration with iodine. Dilute to 200 c.c., add 1 gram of fine antimony powder (chemically pure), and replace on the steam bath, shaking occasionally. A. H. Low uses a coil of sheet nickel, made from a 7 x 1 inch strip of the pure metal, boiling twenty minutes to reduce the tin completely to the stannous condition.

When the tin is completely reduced by one of these pure metals, add a 1 cm. cube of marble to the flask, cool rapidly in running water, keeping the flask covered, then titrate carefully and rapidly with tenth normal iodine, which has been

standardized under the same conditions against chemically pure tin foil.

NOTE. — The foregoing directions apply to samples in which the tin is rather small in amount. When a large amount of tin is present, it is most conveniently separated from antimony, etc., by Thompson's oxalic acid-ammonium oxalate method and electrolyzed (10, Chapter VI).

TITANIUM

13. Titanium is determined in ores and slags by separating it from the bulk of the iron and alumina, converting it with a soda-fusion to insoluble titanate. The titanate is finally dissolved and titanlic hydroxide precipitated from an acetic acid solution in presence of sodium acetate. The *gravimetric* method of A. A. Blair ("Analysis of Iron"), may be adapted to copper products, if the sample is dissolved in acids as for electrolytic assaying, and the copper removed by the electric current. Insoluble residues are fused, as directed in Chapter V. The copper from blast furnace slags may be removed by rapid electrolysis in thirty to sixty minutes. Treat the silica in a platinum crucible with a few drops of sulphuric acid and an excess of hydrofluoric acid, evaporate the latter acid, and preserve. Transfer the electrolyte and solution of residue to a 500 c.c. beaker, evaporate to fumes, and redissolve in 150 c.c. of water. Neutralize the liquid with ammonium hydroxide and add 50 c.c. of strong solution of sulphur dioxide, which should redissolve any slight precipitate. Now pour in a clear filtered solution of 20 grams of sodium acetate and acetic acid (d., 1.04) equal to one-sixth of the total volume of solution. Boil for a few minutes, allow to settle, filter, and wash with 17 per cent acetic acid. Ignite the filter and contents; then fuse this insoluble residue with 5 grams of sodium carbonate for about half an hour. Run the fusion well up on the side, cool, dissolve in water, and filter to extract any soluble alumina.

Wash the insoluble sodium titanate, re-fuse it as before, and cool the crucible. Then pour in very gradually strong sulphuric acid, finally warming the crucible slightly until the fusion is dissolved and fumes of sulphur trioxide are copiously evolved. Pour the fluid contents into 250 c.c. of cold water and wash out

the crucible. Add 50 c.c. of saturated aqueous solution of sulphur dioxide (or 3 c.c. of saturated solution of acid ammonium sulphite), filter if necessary, neutralize with ammonia, treat the clear and almost colorless liquid with the same amount of sodium acetate and acetic acid as before, and precipitate the titanium hydroxide by boiling. If the ignited oxide is still discolored, repeat the fusion and precipitation. Titanium oxide (TiO_2) $\times .6005$ = titanium.

The manner of decomposition and number of purifications for the titanic hydroxide must depend on the material treated. If the original "insoluble matter" contains lead sulphate, this should be extracted with slightly alkaline ammonium acetate before fusion of the residue is attempted.

14. Titanium by Colorimetric Assay.—The color test devised by Weller,¹ and improved by H. L. Wells and W. A. Noyes,² is as follows:

Mix .1 gram of ore with .2 gram of finely powdered sodium fluoride in a platinum crucible, adding 3 grams of sodium bisulphate without mixing. Fuse gently for two or three minutes until copious fumes are evolved. Dissolve the cooled mass from the crucible with 15 to 20 c.c. of cold water, and filter and wash with about 10 c.c. of water. Treat any residue over again in the same way, although the amount of titanium usually found by a second fusion is very small.

To the solution add 1 c.c. of the strongest hydrogen peroxide and a few cubic centimeters of dilute sulphuric acid, when the solution is ready for comparison in a Nessler tube with a standard.

To prepare a standard solution, dissolve pure titanic oxide in hot strong sulphuric acid, add dilute sulphuric acid at first to prevent precipitation, then water until 1 c.c. of the solution contains 1 mg. of titanic oxide, TiO_2 . A new volumetric method has recently been devised by P. W. Shimer.³

ZINC

15. Western Method for Ores and Mattes.—This separation is designed for rapid routine work. The principle involved is the evaporation of the acid solution of the sample and the

¹ *Berichte*, 1882, 2592. ² *Trans. A. I. M. E.* **14**, 763.

³ *Report to Eighth Inter. Congress of Appl. Chem.*

direct extraction of the zinc from the residues by boiling with a large excess of ammonia and ammonium chloride.

Add to a .5-gram sample in a No. 1 beaker 5 c.c. of nitric acid, and cover with a watch glass. When violent action ceases, add 20 c.c. of nitric acid-potassium chlorate mixture. Boil five minutes, then remove the cover, and evaporate to complete dryness. Cool, add 5 to 10 grams of ammonium chloride, 15 c.c. of ammonia, and 25 c.c. of boiling water. Cover and boil two minutes. Filter and wash ten times with a hot solution of 10 grams of ammonium chloride in 1000 c.c. of water, containing a few drops of ammonia. Proceed as described in the estimation of "zinc in slags," beginning with the paragraph, — "Concluding directions."

NOTE. — If the ammonia precipitate is bulky, dissolve it in dilute hydrochloric acid and reprecipitate with ammonia, adding ammonium persulphate and bromine to oxidize iron and manganese. Combine the filtrates and proceed as before. With ores high in manganese, decompose with hydrochloric and nitric acids, and when nearly evaporated to dryness, stir in 4 grams of solid ammonium chloride and proceed as in the following slag analysis. If the solution, after boiling with test lead to remove copper, is yellow or brown from the presence of chlorine or bromine, add 1 to 2 grams of sodium sulphite and boil for a minute more. Dilute the solution to 200 to 250 c.c. for titration.

Some silicate ores require a fusion to obtain all the zinc in solution.

NOTE. — *Zinc in Glass*.¹ It has lately been observed that Jena glass contains zinc compounds which are attacked by alkalies. Such ware should not be used for iron or zinc determinations in refined copper.

16. Zinc in Slags is rapidly estimated, after Western methods, by placing .5 gram of sample (or 1 gram if low in zinc), in a casserole and dissolving in 3 c.c. of water, 5 c.c. of hydrochloric acid, and 2 c.c. of nitric acid. When the silica has completely gelatinized, stir in 4 grams of ammonium chloride. (Some chemists double this amount.) Dehydrate only until the resi-

¹ *E. and M. J.* (1911), 1098.

due crumbles easily, because complete dehydration and baking is liable to volatilize some zinc chloride.

Remove the casserole from the plate and add 30 c.c. of water. Bring to boiling and filter, washing well with boiling water. To the filtrate, add .03 gram of ammonium persulphate and 10 c.c. of saturated bromine water for every .01 gram of manganese in solution, then ammonia in slight excess. Boil two minutes, filter, wash with a mixture of 1000 c.c. water, 100 grams ammonium chloride, and 50 c.c. ammonia, and redissolve the precipitate in dilute hydrochloric acid. Next, add ammonium persulphate, bromine water, and ammonia as before, bring to a boil, and filter. Combine the filtrates from the two precipitations.

Concluding Directions for both (15) and (16). — Neutralize the solution with hydrochloric acid, add 5 c.c. in excess and two grams of test lead, then boil for fifteen minutes. Add 8 to 10 c.c. of hydrochloric acid and titrate, having the temperature of the solution about 60° C. Use ammonium molybdate solution (10 grams per liter) for an indicator, and potassium ferrocyanide as the reagent (32, Chapter III).

The solution has a value of .005 gram of zinc per cubic centimeter and is standardized against pure zinc, or the oxide. At 60° C., the change from bluish white to nearly pure white when the titration is nearly completed, is quite distinct. In the absence of manganese, omit the persulphate and bromine.

17. The Exact Assay of Zinc. — The two following methods, although slower, permit more exact work than the routine works tests already described, especially with minute amounts of zinc. The method of W. George Waring¹ is sufficiently accurate for practical work. In dissolving the sample, all traces of nitric acid, or chlorate, must be removed by evaporation with hydrochloric and sulphuric acids, successively, or by two evaporations with the last acid to abundant fumes. Dissolve in 25 to 40 c.c. of water, add enough sulphuric to bring the free acid to 10 or 15 per cent by volume. Introduce a piece of heavy sheet aluminum, and boil ten minutes, or to complete reduction. Filter and wash through a filter containing a piece of aluminum into a beaker containing a strip of the same metal. Cool, add a drop of methyl orange, and neutralize carefully with sodium

¹ *J. Am. Chem. Soc.* **29**, 265.

bicarbonate to a light straw color. Add dilute 20 per cent formic acid, drop by drop, until the pink color is just restored, then 5 drops more. Dilute to 100 c.c. for each .1 gram of zinc; add (if much iron is present) 2 to 4 grams of saturated solution of ammonium thiocyanate, remove the aluminum, heat to boiling, and saturate with hydrogen sulphide gas. Allow the pure white mass to settle for a few minutes and then filter.

A more rapid separation of the sulphide of zinc may be secured by passing the glass delivery tube through a rubber stopper, which fits loosely into an Erlenmeyer flask containing the solution. As soon as the solution is saturated with hydrogen sulphide, jam the stopper down while the gas is passing, producing a slight pressure which causes a quick subsidence of the white precipitate. Transfer the filtered and washed sulphide with the paper to a capacious beaker, heat with 8 to 10 c.c. of strong hydrochloric acid until dissolved, add water and titrate the zinc. The hydrogen sulphide must be expelled by heating before titration. A 1 per cent solution of ammonium heptamolybdate is recommended as the indicator. Only a part of the cadmium deposits on the aluminum, but the percentage of this element in copper ores is generally so low that it may be counted with the zinc.

18. Proposed Standard Method for Zinc.—F. G. Breyer recommends that 1 gram of ore (or .5 gram if over 50 per cent zinc) be dissolved in a tall 150 c.c. lipless beaker, covered, by 10 c.c. of hydrochloric acid and a little water. (Jena glass should be rejected from such work, as it contains zinc.) A sample is taken at the same time and dried at 110° C. for moisture determination. After boiling one-half hour remove the cover, add 10 c.c. of sulphuric acid, and evaporate slowly to strong white fumes, breaking up the silica if necessary. Then dilute to about 40 to 50 c.c. and add about 1 gram of aluminum powder, cover, and boil until colorless, which requires ten to fifteen minutes.

If the cadmium in ores is uniformly less than .05 per cent, it is allowed for, or counted with zinc, as in **17**. A separation of cadmium should be made, if an accurate result on zinc is desired. (Method 14, Chapter VI, also precedes this separation).

(a) The cadmium not reduced by aluminum is thrown down by hydrogen sulphide after adding 5 c.c. of (1:1) sulphuric acid and diluting to 100 c.c. Neutralize until cadmium sulphide

appears, and heat to 70 to 90° C. Filter, wash with cold 8 per cent sulphuric acid, then with hot water, first closing the paper with precipitated sulphur. Dissolve and evaporate to fumes with sulphuric, adding any reduced cadmium.

(b) The cadmium may then be electrolyzed, after the addition of 1 c.c. of (1:1) sulphuric acid to the carefully neutralized solution.

Total volume 100 c.c.; current .8 to 1 ampere per square decimeter of cathode surface; time one and one-half hours at 2.95 to 3.05 volts with a coppered cathode, — the best is a gauze electrode coated with cadmium over copper, which may be used repeatedly.

(c) The zinc solution is then boiled to remove hydrogen sulphide, exactly neutralized with potassium hydroxide, finishing with sodium bicarbonate, and then made acid again with 2 to 4 c.c. of 5 per cent sulphuric acid in excess for each 100 c.c. of solution. The zinc is finally precipitated, redissolved, and titrated as in **17**, with potassium ferrocyanide having a value of 10 mg. of zinc per cubic centimeter. This solution has a temperature coefficient sufficient to decrease the factor .2 per cent for 5° C. rise in temperature; hence any variation between the temperature of standardization and actual analysis should be corrected.

This modification differs from Waring's method (which the author prefers) in the fact that sulphuric acid is used instead of formic, and the aluminum is taken as a powder.

19. European Method for Zinc in Mansfeld Ores. — These ores carry nickel and cobalt with the zinc. Hermann Koch separates the former elements from zinc by direct precipitation with hydrogen sulphide in a faintly acid sulphate solution, as in **18**. The purified sulphide is finally ignited in a Rose crucible in a stream of hydrogen.

The author also recommends titration by standard sodium sulphide, shaking the solution in a flask with a layer of carbon tetrachloride.

The sodium sulphide is protected from oxidation by keeping the space above the stock solution charged with illuminating gas (meeting an objection of Mr. Waring), but the process, although claimed to be well adapted to lead, has not found favor in the United States.

FURNACE REFRACTORIES

20. Beach-sand, or quartz for converter lining, containing over 95 per cent silica, is treated to best advantage if the silica is at once volatilized.¹

Weigh at least 1 gram of the fine powder (ground in agate), and treat it in a weighed platinum crucible, with a few drops of strong sulphuric acid, placing the crucible upon a pipe-stem triangle, resting on a wire gauze. Add gradually enough hydrofluoric acid to dissolve the silica, then evaporate in the hood with the heat of a Bunsen burner, and heat to redness long enough to decompose the ferric sulphate. Weigh the residue, and later correct it by deducting the weight of sulphur trioxide, calculated to exist in combination with the calcium, magnesium, and alkalies. Fuse the slight residue with sodium carbonate and determine the alumina, calcium, and magnesium oxides by the regular methods given for slags in method 10, Chapter V.

The determination of alkaline metals is given in a succeeding paragraph, but for ordinary purposes it is sufficient to estimate the bases, already mentioned, and deduct their sum from 100 per cent to obtain the silica.

21. Semi-fusible Sand, of lower silica content (90 to 95 per cent), derived from weathered feldspathic rock, is employed at Lake Superior, Michigan, and elsewhere, to render pure sand more fusible. Such sand requires fusion with dry sodium carbonate and a trace of sodium nitrate, after which the mass should be dissolved in dilute hydrochloric acid and dehydrated twice by evaporation to dryness with an intermediate filtration. The bases are determined as in the analysis of reverberatory slags and calcines, Chapter V, or as in the analysis of clays. Alkalies are determined by methods 6 to 9, Chapter VII.

ANALYSIS OF CLAYS

22. Fire-clay, or fusible clays, are usually dried before use as a fettling material, and then ground. An average sample may then be taken.

Any residual moisture is determined by drying a sample at 100 to 105° C. To obtain the loss on ignition, which is mostly

¹ Original method due to A. A. Blair.

due to water of composition in the hydrated silicates, ignite a sample of 1 gram in a platinum crucible to a constant weight.

For bases, fuse 1 gram of dried clay with 10 grams of sodium carbonate and a pinch of pure sodium nitrate. Transfer the fused mass by means of hot water to a platinum dish. Clean the crucible with a little hot hydrochloric acid, make the solution acid with hydrochloric acid, and evaporate twice to dryness at 100 to 105° C. with the addition of dilute hydrochloric acid before the second evaporation. Dissolve in 10 c.c. of the same acid, add 50 c.c. of water, filter the silica on an ashless paper, ignite, and weigh. Treat the weighed residue with two drops of sulphuric acid and an excess of hydrofluoric acid, evaporate, ignite, and weigh again. Deduct the weight of the last residue from that of the total siliceous matter to obtain the true weight of pure silica. Fuse the last residue with the least possible amount of potassium bisulphate, or sodium carbonate, and return the solution of the melt to the main solution of the bases. Determine the bases by the methods recommended for slags and ores, 5-12, Chapter V. If potassium and sodium are required, refer to methods 6-9. If extremely accurate results are desired, the work should be performed in platinum dishes. It would be necessary to grind all such refractory siliceous material in agate, or in porcelain ball-mills, after it leaves the crusher.

CHROMIUM COMPOUNDS

23. Complete Analysis. — Chromium and iron in chromite or furnace refractories may be estimated by the volumetric method of A. G. McKenna.¹ The material should be ground (after coarse crushing) in an agate mortar to pass a sieve of 100 meshes to the linear inch (40 per cm.). Fuse .5 gram of the powder in a nickel crucible at a low red heat for one minute, or until decomposed, and determine the chromate in the solution of the fusion by method 15, Chapter VI.

Iron. — Dissolve the iron from the insoluble residue with (1:10) sulphuric acid, reduce it with zinc or with slight excess of stannous chloride and titrate with potassium permanganate (6-7, Chapter V.) Calculate to ferrous oxide, FeO.

Silica and bases may be determined in a second sample by a modification of the method of McKenna. Fuse .5 gram

¹ *Proc. Eng. Soc. W. Pa.*, **16**, 119 — *Methods of Iron Analysis*, Phillips, **156**.

of the powder in a silver crucible with 4 grams of pure sodium peroxide. Just as soon as fusion is complete, cool the crucible and dissolve the melt in water in a 3a casserole. (If alumina is to be separated from chromium as noted in the final paragraph below, boil for ten minutes to destroy peroxide which might cause premature reduction of the chromium after the solution is acidified.) Filter the liquid from the undissolved portion. The residue contains iron oxide, magnesia, a little silver, and silica. The filtrate should contain the chromium, alumina, and most of the silica.

Residue. — Dissolve the insoluble portion in an excess of nitric and sulphuric acids, cleaning the crucible with the latter acid. Evaporate to fumes, take up with water, and filter off the silica. To the solution add two or three drops of hydrochloric acid and filter off any trace of silver chloride which may separate on stirring. Precipitate the iron hydroxide by ammonia, ignite, and weigh. The ferric oxide may contain traces of alumina. To the filtrate add ammonium oxalate, filter off the calcium oxalate, and remove the magnesium as phosphate (10, Chapter V). Nickel and zinc, if present, are separated before the lime, the nickel by dimethyl glyoxime (5, Chapter VII), and the zinc by saturating the filtrate with hydrogen sulphide after acidifying with a slight excess of acetic acid.

Filtrate from Peroxide Fusion. — Acidify the solution of sodium aluminate, chromate, and silicate with hydrochloric acid and evaporate to dryness. Dilute, filter off the silica, and evaporate again to dehydrate the last traces of silica. Ignite the washed silica with that obtained from the insoluble residue. Test its purity with hydrofluoric acid. Precipitate the aluminum and chromium as hydroxides from a boiling solution with a slight excess of ammonia. Filter, wash thoroughly, ignite and weigh. To obtain the alumina, deduct the weight of chromium sesquioxide calculated from the titration.

An approximate separation of aluminum from chromium may be effected, if desired, by treating the alkaline filtrate from the original fusion as follows:— Acidify with nitric acid, evaporate to dryness on a water bath, dissolve in nitric acid, dilute, and filter off the silica. Test the filtrate for silver with one drop of hydrochloric acid, filter and wash. Make the solution slightly ammoniacal, warm until coagulated, and filter, washing four times back and forth from beaker to filter with water and a

trace of ammonia. Ignite and weigh. Reduce chromium in the filtrate by evaporating to dryness with an excess of hydrochloric acid.

Take up with hydrochloric acid and evaporate again to remove all the nitric acid and completely reduce the chromium. Finally, throw down the chromium hydroxide with an excess of ammonia.

CHAPTER VIII

FIRE ASSAYING FOR LEAD, SILVER, GOLD, AND PLATINUM IN ORES AND FURNACE BY-PRODUCTS

Commercial Requirements.¹ — In most transactions involving the purchase and sale of argentiferous copper materials, the so-called "commercial assay" governs financial settlements. The term commercial assay means the usual fire or combination assay, without including corrections for gold or silver which could be recovered by reassaying slags and cupels.

Corrected assays are made only when contracts require them. Deductions for refining, or refining charges, are generally based on commercial assays, and these bear a very constant ratio to corrected assays for any given material. (This ratio is so uniform that E. Keller uses the slag and cupel correction for a month's run on Anaconda anodes as the correction for the next month's copper.) Corrections are obtained by reassaying the cupels and slags, and adding the silver and gold recovered. Manuals of assaying have described, in detail, the testing of true gold or silver ores. This chapter treats only of native copper, or copper ores smelted at copper reduction works, and the furnace by-products.

Systems of Assay Weights. — On the European continent assay results are calculated in "grams per kilo," or "grams per metric ton of 1000 kg." 1 metric ton equals 2204.6 pounds avoirdupois.

In Great Britain, we find results expressed in Troy ounces per ton of 2000 pounds, the long ton of 2240 pounds being often used.

Assayers in the United States have almost entirely adopted the so-called "Assay-ton system." The concise definition of Dr. A. R. Ledoux explains the system.

"Silver and gold are reported in Troy ounces (of 480 grains each), per ton of 2000 pounds avoirdupois. One such ton contains 29,166.66

¹ A. M. Smoot, personal communication.

ounces Troy. The 'assay-ton' (A. T.), a weight introduced by Dr. C. F. Chandler, contains 29,166.66 milligrams; hence each milligram of silver or gold, obtained by assay from 1 A. T. of sample, represents 1 ounce Troy per ton of 2000 pounds. The ounce Troy is equivalent to 31,103.49 mg., and one ounce per ton, as above, equals 34.286 grams per metric ton or .00343 per cent."

ASSAY OF LEAD

1. The Dry Lead Assay. — According to "Western practice," a *lead-flux* stock mixture is made up in large quantity as follows: sodium bicarbonate 64 parts, powdered borax 16 parts, argols (crude cream of tartar) 14 parts. Mix 10 grams of sample with 20 grams of "flux," cover with 10 grams more flux. Put in 3 nails, then a cover of 1.5 inches (3.8 cm.) of salt (sodium chloride). Oxide and carbonate ores, as well as those high in zinc, require the addition of some borax glass, but only the amount necessary to give a good pouring fusion must be used or the slag will be too acid and carry off lead. Place the crucible in a good hot muffle and close the door. As soon as the salt cover is melted and the argols begin to flame, shut off the draft and lower the heat to a little below scorifying temperature. Keep at this heat until flaming of argols ceases, then raise the temperature to the highest heat possible, and pour. The pot furnace may be used instead of muffles. The "wet methods," especially titration, involve more work, but are much more accurate than the fire assay, especially on cupriferous ores.

GOLD, SILVER, AND PLATINUM

2. Gold and Silver, in Colorado, are generally assayed by the scorification method, but in Arizona, California, Michigan, and Montana ores are more often fired in crucibles. If the copper percentage is sufficient to class a sample with copper ores, the calculated niter assay, or the excess litharge flux, is adopted. If the ores are low in copper, arsenic, or antimony, good results may be obtained by the method of Aaron, using iron nails as the desulphurizer.

If fused sodium carbonate is employed, take only 60 per cent of the amount in the table. An assay furnace has been described in Chapter I. The best crucibles for gold and silver assay are the Denver, or Battersea, but the cheaper Hessian sand crucible is favored for the fire assay of native copper, where it is

necessary to clean the button from iron. Place the assays in the muffle, or pot furnace, at a good red heat, fill in coke around the crucibles, and bring the heat up gradually until there is no more danger of loss by foaming, after which the tests are brought up to a high heat and quiet fusion, then poured into iron molds, the insides of which are painted with iron oxide (*crocus*).

As this account presupposes some knowledge of principles, the reader is referred to Brown's "Assaying," ninth edition, page 185, or to Lodge's "Notes on Assaying," for the general details of melting and cupellation. Less reducer is required if the crucibles are kept covered in the furnace. The proportions of flux and reducer must be adjusted to the conditions of the sample and firing. The amount of sulphides is roughly determined, accordingly, by vanning some of the sample. If the

FLUX FOR IRON NAIL METHOD

Crucible Assay	A-1 Quartz oxidized	A-2 Ore with little iron sulphide	B Half gangue Half sulphide	C Mostly iron sulphide
Sample taken	3 A. T.	1 A. T.	1 A. T.	1 A. T.
Litharge.....	100. gr.	35-50 g.	35 g.	35 g.
Sodium bicarbonate.....	125 fused	60-100	60	50
Borax glass.....	50	5-30	10	20
Argols (or 75 % of flour).....	2-3	2
Silica, fine.....	5	10
Iron, 20 penny nails.....	1	4

Cover—2.5 to 3.8 cm. of salt, sodium chloride.

lead buttons are hard enough to crack, or split, when squared on the anvil, they should be scorified before cupellation with the addition of a little more lead, unless the button is very large.

Cupellation.—The lead buttons, when rendered sufficiently pure by scorification, are dropped into hot marked cupels placed in the hot muffle, the door closed and the assays brought to the front, or the heat lowered as soon as the assays are melted down.

The lead is allowed to vaporize in the open muffle at a heat low enough to cause the cupels to "feather" nicely. (It is best to round off the corners of the lead buttons, which will weigh,

according to the ore and flux, from 10 to 20 grams.) When the lead is nearly gone, and the play of colors, known as the "blick," is about to appear, the button becomes round and the litharge commences to swim over the small button. At this point the button should be pushed into the hottest part of the muffle. Soon after the blick, the assay should be withdrawn from the muffle, covering the bead with an old cupel, if necessary, to prevent any sprouting of the button. It is never safe to accept a sprouted button. Cement-lime, or "Brownite" cupels are much used at present, instead of bone-ash, especially by Lake Superior refineries for the direct cupellation of silver chloride in the assay of anodes, Chapter IX. These cupels must be ignited at a low yellow heat and brought to a low red heat before the lead buttons are introduced, in order to prevent spitting. With this precaution, this cupel will absorb less silver than bone-ash, particularly when silver chloride is directly cupelled with powdered lead. The calcium oxide of the cupel assists in the prompt reduction of the chloride, preventing loss by volatilization.

Weighing and Parting for Gold. — The beads are separated by forceps, brushed with a stiff brush, and any adherent material removed by very careful picking with a needle, or by dipping the buttons in very dilute hydrochloric acid. The weights on a gold balance should, of course, be carefully adjusted from time to time to detect any variation. If only gold is to be weighed, the beads are transferred at once to small porcelain crucibles, or test tubes, and heated nearly to boiling with dilute nitric acid. Assayers vary in the strength of acid specified. The Western contributing chemists recommend an acid as dilute as 1 volume of acid to 9 of water for the first treatment. When the action ceases, a few drops of strong nitric acid (d., 1.42), are added and the warming continued for a few minutes. The crucible is then filled with hot water repeatedly, tapped, and poured off.

Estimation of Platinum. — This metal dissolves quite completely in nitric acid in the presence of 8 parts, or more, of silver. The silver beads, containing platinum, are parted by boiling for about fifteen to twenty minutes with a little strong sulphuric acid. The purified gold and platinum are washed, annealed, weighed, then remelted with 8 to 10 parts of pure silver foil, and parted a second time with nitric acid (1:1) to dissolve the silver and platinum, leaving the gold for weighing.

A more accurate *special* method is given in the latter part of this chapter.

2a. Excess Litharge-Assay for Gold. — Ledoux & Co. assay rich sulphides, mattes, or slags as follows: Mix one-half assay ton (A. T.) of sulphides in a G crucible with 500 grams of flux, composed of litharge 40 parts, soda 4 parts, silica 4 parts, adding a salt cover. For slags use only 300 grams of flux. Fuse for about thirty minutes, starting at a low heat and raising the temperature gradually during the first twenty minutes, then withdraw the assay, cool and break the crucible. The lead button, reduced by the sulphur and iron, will weigh from 80 to 100 grams. Scorify the button to about 30 grams weight before cupellation. Cupel and part as in the scorification method for gold (method 4).

When the material for assay is low in gold, make a number of crucible fusions, using .5 A. T. charges of ore in each. After reducing the large lead buttons by scorification to about 30 grams each, unite several, and scorify to a single button of a size suitable for the cupel. Usually, four crucible fusions, representing two assay tons, are sufficient.

If the material under assay is deficient in silver as compared with gold, some silver may be added to the crucible or scorifier. A very large amount of litharge flux is essential in assaying matte and ores rich in copper. This method is very satisfactory for gold, but it cannot be relied upon for silver. For mattes, the combination method 5 is generally the most satisfactory. When silver is added, it should be six or seven times as much as the gold present.

Cupellation. — The cupellation is made at a low heat and the beads parted for gold as described in the combination method for metallic copper (5, Chapter X).

The addition of silver, as recommended, reduces the slag and cupel losses of gold and facilitates parting. The above is an excellent process for gold in mattes, but on account of the lengthy scorification, the silver is apt to be too low, and even when no silver is added, the results on that element are useful only as a rough check on some other method. W. G. Perkins¹ advocated a similar litharge process in 1901, but reduced the weight of sample with increase of copper.

¹ *Trans. A. I. M. E.* 31, 931.

2b. Western Soda-Niter Method.—Niter as a powerful oxidizer is preferred by many chemists in western copper works, as it lessens the quantity of litharge. The reducing power of each class of ore must be known beforehand. On unknown ores, this may be tested by a preliminary fusion of 3 grams of ore with the following charge: litharge 50 grams, sodium bicarbonate 10 grams. One gram of niter oxidizes 4 to 4.7 grams of lead to oxide, and 1 gram of flour will reduce 10 to 10.5 grams of litharge to metallic lead. A good charge for the final assay is .5 assay ton of ore, 70 to 100 grams of litharge, 15 grams of sodium bicarbonate, and sufficient niter to produce a 20-gram button.

The trial assay is avoided in regular daily tests of metallurgical products of copper reduction works, because the general character of the samples is known. A general idea of the proper composition of assay charges for such products may be obtained from the table and used as a basis for experimental assay of unknown material.

The fluxes are given for samples of 1 A. T. (29.167 grams).

CRUCIBLE METHOD

Product	Per cent Cu.	Per cent sulph.	Lead oxide	Sodium bicarb.	Powd. silica	Flour	Potass. Nitrate	Cover
Ores —								
Calcined,	6-9	8-15	grams. 80 to 100.	grams. 50	grams. 5-15	grams. 0-.5	grams. 0-8	Thin borax or 1" salt
Flue dust. .								1" salt
Mill conc. and slimes.	4-10	5-40	150	35	10	0-	10-40	
Raw sulphides	2-15	15-30	150	35	10	0	10-40	1" salt
Fur. slags.3-2.0	.5	80	50	..	.2-4.	0.	salt or borax

Correction for Cupels and Assay Slags.—This is only made when there is an agreement between the parties in a contract, and is determined in ordinary cases on each class of material smelted. Papers by several authors have shown that as the size of silver beads is increased the percentage loss of silver by cupellation decreases. The loss on a 20 mg. bead may be 3 to 5 per cent of the original silver, but on a 100 to 150 mg. bead will be only 1 to 2 per cent.

To make a correction for loss in firing, the leady portion of cupels is ground to pass a $\frac{1}{30}$ -inch screen, a pair of checks being fused as one sample. The silver loss in a scorifier slag is usually small, .1 to .2 ounces per ton. Crucible and scorifier slags are ground to pass a $\frac{1}{20}$ -inch screen, fused in crucibles at a high heat, and the buttons cupelled, weighed, and parted for gold.

Charge in Grams (1 inch salt cover)	For 2 cupels	For 1 A. ton of slag	For 2 A. ton of slag
Litharge.....	30 grams	20	40
Fused soda carb.....	20-30 "	15	30
Borax glass.....	30-60 "	0	0
Cream tartar.....	2- 5	2	2

Temperature of Cupellation. — Lead melts at about 100° below silver chloride, or at a muffle temperature of nearly 326° C. (Rose). Litharge freezes at 840°, or when the cupel is at 907° according to Bradford. R. W. Lodge recommends a muffle temperature of 625 to 800° C. Refer to papers on pyrometry.¹

2c. Fusion with Sodium Peroxide. — Wells and Burrows² have proposed a change in the regular soda-niter assay, **2b**. Sodium peroxide is adopted as the oxidizer of sulphides, or arsenides, instead of niter, or as a substitute for the roasting process. Sodium peroxide used with iron nails will eliminate 50 per cent of sulphur from pure pyrites. The loss of gold or silver is said to be no greater than with niter. This is a promising suggestion, although the additional expense would prohibit its use, probably, in custom work.

SCORIFICATION

The objection to the following methods, which are yet specified in some agreements in the United States, is the small quantity treated and the increased fire loss in silver which repeated treatments involve. Such methods are better for gold in metallic copper or matte, higher results being obtained for silver in metals by the combination of "wet and dry assaying."³

3. Western Method for Matte. — The usual limits are, copper 30 to 55 per cent; silver 30 to 200 ounces per ton; gold .1 to .4 ounce.

¹ F. P. Dewey, *J. Ind. Eng. Chem.* **6** (1914) 405.

² *Trans. A. I. M. E.* **34**, 387.

³ Note by A. M. Smoot, Ledoux & Co.

Scorify .10 assay ton (3 grams) of matte in a 2.5-inch (6 cm.) scorifier with 60 to 80 grams of lead, .5 gram of borax glass, and a little silica. This gives a 35-gram button. Cupel and weigh the silver with gold, then part as in the crucible methods, and weigh the gold.

Open the scorification at a high heat and continue at a moderate temperature. It is often necessary to rescorify with more lead.

4. Silver in Clean Mattes and Low-grade Ores.—Although the following process is frequently specified for silver at the port of New York, it is not considered reliable for gold, because the charge is too small and there is considerable loss in cupellation.¹

Mix .1 A. T. of sample with 35 grams of test lead in a 3-inch scorifier, add 35 grams more lead as a cover, and add about 1 gram of borax glass. Scorify as already directed and, if the button is soft, cupel directly. If the button is hard and contains considerable copper, as will be the case with rich ores and mattes, make the weight up to sixty grams by the addition of test lead and rescorify before cupeling. At least five assays should be made on each sample and the beads united for parting.

5. Gold Only, in Mattes.²—The assay is similar to that for metallic copper given in the next chapter. Weigh four portions, each of .25 A. T., into four 3-inch Bartlett scorifiers together with 85 grams of lead for each portion. Mix two-thirds of the lead with the matte and use the remainder as a cover, adding to each assay two grams of borax glass. Open the scorifications very hot, as in 3, and then continue at a moderate heat until the slag covers over. The lead buttons should weigh about 30 grams each. Unite them two and two, add a little silica, and scorify again in new scorifiers to obtain 15-gram buttons. Make each of these up to 90 grams by the addition of test lead, add a little silica, and scorify again to obtain 30-gram buttons, which should be practically free from copper. Cupel at a low heat and part for gold as described in the nitric acid combination method for metallic copper, Chapter X.

In assaying material containing a large amount of gold in proportion to the silver, it is necessary to add silver to the first scorifier so that the silver shall be six or seven times as much as the gold present. The silver addition reduces slag and cupel

¹ Note by A. M. Smoot.

² From A. M. Smoot.

losses and facilitates parting. This is an excellent method for gold in matte, but on account of the repeated scorifications, the silver is apt to be low, and even when no silver is added, the results on that metal are useful only as a rough check on some other process.

6. Combination Assay for Silver (and Gold) in Mattes. — This method has been used everywhere for mattes and copper, but it gives low results on gold owing to the solution of a small part in the nitric acid.¹

For this reason, metallic copper is more generally tested by the "mercury-sulphuric acid" method (Chapter X), or by the bisulphate method (8) which requires rather more time and attention. A. M. Smoot prescribes a test which is the most satisfactory for silver in mattes, especially when the material contains much bismuth.

Treat one A. T. of sample in a 600-c.c. beaker with 100 c.c. of water, add 30 c.c. of sulphuric acid (d., 1.84), a little at a time, if the matte is high in iron; otherwise the evolution of hydrogen sulphide may be so violent as to cause loss. When most of the sulphide of iron has been decomposed, boil the solution to eliminate all hydrogen sulphide. By this means a large part of the sulphur is expelled, and operations facilitated. To the hot solution, add 100 c.c. of nitric acid in small portions until the copper is dissolved. Heat if necessary, dilute with water to 400 c.c., and filter. Wash the beaker, wipe it carefully with filter paper, add this to the filter, and reserve the filtrate and washings.

Scorification. — Transfer filter and contents to a litharge-glazed scorifier, dry and burn the filter, best in a closed oven. Add test lead to the residue and scorify it so as to obtain a 10-gram button, which is cleaned and reserved. The size of the scorifier and quantity of test lead will depend on the amount of insoluble matter.

To the filtrate, add sodium chloride solution sufficient to precipitate all the silver, and stir it until the silver chloride agglomerates. Small amounts of silver require the addition of about 3 c.c. of concentrated lead acetate solution to form lead sulphate as a collector. Let the silver settle — best over night — and filter on double close filters. Wash the beaker and wipe

¹ *J. Amer. Chem. Soc.*, **31** (1910), 318 and 1262.

it thoroughly with filter paper, adding this to the residue. Transfer the filter and contents to a 2.5-inch litharge-glazed scorifier and calcine in a closed oven until the paper is charred. Remove to the open air and the remaining carbon will glow gently until consumed. Now add the first button obtained, together with enough test lead to bring the total weight of lead to 30 grams. Scorify, cupel, weigh, and part as in the nitric acid method for copper (Chapter X).

NOTE. — Silver chloride has a melting point about 100 degrees above that of lead. The chloride should therefore be reduced at a low temperature not over the melting point of lead, to prevent vaporization. Loss may be further prevented by dusting about 1.5 grams of the powdered lead on the inside of the filter before charring.

7. Combination Assay of Mattes Containing Lead. — Mattes containing lead are not decomposed by sulphuric acid sufficiently to make that step worth while; moreover, the large amount of lead sulphate formed renders the filtration difficult. If the acid method is to be used, Smoot treats one assay ton of sample with 150 c.c. of nitric acid (d., 1.42), adding it slowly until decomposition is complete. Boil, dilute to 450 c.c., and proceed exactly as in 6.

8. Special Assay for Gold, Silver, and Platinum in Rich Ores and Mattes. — To avoid the loss of gold due to nitric acid, and to permit the exact separation of the valuable metals, the author makes use of sulphuric acid only, adding a reagent to facilitate solution which has no injurious effect.

Although the combination assay, as applied to ores, involves too much manipulation for custom work, it has proved valuable for the exact assay of rich material, such as mattes and native copper. The metals in the insoluble residue may be collected with very little litharge, avoiding the large slag loss of the direct fire assay.

Solution of Ores and Mattes. — Weigh out 1 assay ton (29.167 grams) after grinding the sample to pass a sieve of 60 meshes to the linear inch. With native copper, prills or nuggets may have to be removed and separately tested. Place the material in a No. 4 casserole. Then add 30 grams of solid potassium

bisulphate, mix well, and withdraw the glass. With mattes, 10 grams of sodium peroxide have been occasionally introduced as an oxidizing agent.

In either case, add very slowly to the covered casserole 50 c.c. of sulphuric acid (d., 1.84). Heat very slowly in the hood with a Bunsen burner, taking care that the heat is not high enough to carry the mixture up to the cover. About five minutes' gentle heat will usually decompose the mass so that the acid will boil quietly under the cover and the sulphur will distill and collect on the under side of the glass. Without moving the cover, pour in 30 c.c. more acid and boil hard for half an hour. At the end of this period, the sulphur should all be boiled out of the casserole, except possibly two or three globules. If preferred, these may be removed by longer boiling after washing down with a few drops of strong acid. Now dilute the cooled mass of sulphates with water and heat to dissolve soluble salts. Stir rapidly and add enough hydrochloric acid to precipitate any dissolved silver. Dilute to 500 c.c. and transfer to a 750 c.c. beaker. Allow to settle for fifteen minutes and filter.

Place in a small clay crucible the following fluxes: 30 grams of litharge, 30 grams fused sodium carbonate, 10 grams potassium carbonate, 10 grams borax glass, and .6 gram of flour, or enough to reduce a 12-gram button of lead. Dry the filter, shake out the contents carefully on top of the mixed flux, char the filter with an inverted burner, stir with a rod, cover with a 2.5 cm. layer of salt, melt, and pour as usual. Cupel the buttons at a heat low enough to feather properly. The slag loss is low, and the residues from three or six solution assays may be combined and fused in a crucible as one siliceous ore. The F. F. Hunt Laboratory, New York, uses a mixture of sodium sulphite and sulphuric acid for the same purpose.

SEPARATION OF SILVER, GOLD, AND PLATINUM

9. Direct Method of Separation. — At the Rambler Mine, the procedure is as follows:¹ Eight portions of one "assay ton" each are generally weighed into 20-gram crucibles for fusion, although the quantity of sample depends on the richness of the product. If much copper is present, the buttons are rescorified

¹ A. C. Dart, *Met. and Chem. Eng.* **9**, 75; **10**, 219.

until soft and then cupeled. Thus far the preceding method could be employed to advantage.

When the total precious metals have been weighed, they are combined in two check lots, representing four assay tons each, and are then cupeled again with ten times their weight of pure silver. The resulting buttons are parted separately with 12 per cent nitric acid, and finally in strong nitric acid in test tubes placed in boiling water. Silver, palladium, and platinum are thus dissolved and gold remains. The residue is now washed in the usual way, and the gold ignited and weighed. The nitric acid solution from the preceding step is kept as small in volume as possible.

The silver is separated by precipitation as chloride, which is filtered off and washed free from acid.

Platinum and palladium are obtained from the filtrate, which is evaporated to dryness, and redissolved in a few drops of hydrochloric acid and 10 c.c. of hot water. This solution is allowed to stand for half an hour, and if silver chloride separates, it is again filtered and washed, the precipitate being combined with the first obtained. The filtrate is now made ammoniacal, then acidified with formic acid and boiled. This will precipitate metallic platinum and palladium, which are filtered, or washed by decantation, ignited, and weighed.

Separation of Platinum and Palladium. — The weighed metals are converted into chlorides by dissolving in aqua-regia, evaporating to dryness, and taking up with a few drops of hydrochloric acid and 50 c.c. of hot water. This solution is saturated with pure crystallized ammonium chloride; 10 c.c. of alcohol are added, and the whole allowed to stand not less than twenty-four hours. The ammonium platinic chloride is then filtered, washed with a saturated solution of ammonium chloride, and ignited very slowly to prevent loss of metal. The resulting platinum is weighed and the gold having been already directly weighed, the silver is obtained by difference. If a trace of platinum is sought, reduce the volume. Palladium, if present, is determined by the difference between the combined weight of palladium + platinum, and the platinum precipitated by ammonium chloride.

It is generally considered that more than one fusion of gold with ten parts of silver is required to remove every trace of platinum. Unless the platinum is considerable, the old way of

parting with boiling sulphuric acid — taking the weight of gold with platinum, and then remelting with excess of silver and parting with nitric acid for gold — gives uncertain figures on the platinum calculated by difference, unless the gold is also very small in amount.¹

10. Indirect Method.² — All the platinum (after parting the silver with nitric acid) may be removed from solution by a partial precipitation. The gold is first removed by decantation, or better, by filtration. The essential details are as follows: Small amounts of platinum will readily dissolve in nitric acid with the silver. If now a limited amount of hydrogen sulphide water be added to the solution from parting, any platinum present will be precipitated as sulphide, along with some silver sulphide. After filtering and slightly washing, the moist filter is transferred to a small porcelain crucible, dried at a low heat, and burned off by gentle ignition. This transforms the platinum to a metallic sponge, which is wrapped in a small piece of lead foil and cupeled. The resulting bead is then parted in strong sulphuric acid, when the platinum will be left as a dark residue, generally in spongy form even when minute in quantity. This sponge, after reboiling in fresh acid, if necessary, is suitably washed by decantation, annealed, and weighed. The platinum may be dissolved in a drop or two of aqua-regia and gently evaporated. The solution obtained may be tested with potassium iodide, or a few small crystals of ammonium chloride may be added when the characteristic precipitate will show itself. This may be filtered off and gently ignited. If considerable, the platinum may be determined by the double-chloride method. Any decided difference shown would indicate the presence of other members of the platinum group, for which a direct test could then be made.

NOTE (on hydrogen sulphide treatment). — A very dilute solution should be used, diluting the saturated solution with about 15 parts of water, and using 15 c.c. of the diluted reagent for an ore, or 30 c.c. for a bullion. The reagent should be added very slowly to the silver nitrate solution with constant stirring. The solution should darken, but not visibly precipitate. The solution

¹ Second Method — *Met. Chem. Eng.* **12** (1914) 481.

² Method of F. P. Dewey. See method of Smoot, *Eng. & Min. J.* **99** (1915) 700.

should be stirred occasionally for two hours, when flocks should appear, which may be filtered off in 3 to 4 hours, although it is better to settle over night.

If only minute amounts of platinum are present, it is still necessary to add sufficient hydrogen sulphide to give a silver bead large enough to handle comfortably. It may happen that the final metal shows the yellow color of gold, due to the fact that exceedingly fine float-gold passed over in decanting. In such a case the metal must be realloyed with silver and the treatment repeated. When the proportion of gold to the silver in the metal being parted is so small that the gold separates in a finely divided state, it will often save trouble to filter the silver nitrate solution, before adding hydrogen sulphide.

NOTES. — Coin silver may also be tested by this method, taking about 100 grams, evaporating the nitric acid solution nearly to dryness, and treating with 5 c.c. of strong hydrogen sulphide, diluted to 50 c.c. Much platinum, alloyed with silver, is not entirely soluble in nitric acid. Hence the operation of alloying the gold with silver and parting must be repeated a second, or even a third time, when such material is assayed.

For the separation of the rarer elements of the platinum group, occurring in minerals, refer to the report of the international committee on analyses to the Eighth International Congress of Applied Chemistry, pp. 1-24.

THE FIRE ASSAY OF NATIVE COPPER

11. Lake Superior Method. — The refineries of northern Michigan employ as an alternative or substitute for the electrolytic method, a short direct fire assay, which is only successful in the entire absence of sulphur and sulphates from the ores or chemicals.¹

The description of this process is condensed, as it is only of local interest. The materials subjected to fire assay are:— (1) Rich "cover" work, or coarse heading from the mortars, about 90 per cent copper; (2) finer mill concentrates from jigs, containing 65 to 90 per cent copper; (3) slime concentrates, from revolving or shaking tables, 20 to 30 per cent copper. The ideal would be attained if the copper could all be reduced into a

¹ *J. Am. Chem. Soc.* **24**; *Eng. and Min. J.* 1895, 369.

button in one short fusion, without a simultaneous reduction of some iron into the button. As most of the arsenic enters the refined metal, it is reduced and weighed with the copper as far as possible. Concentrates (over 40 per cent copper) are so fluxed and fired that the loss of copper in the slag is limited to about .25 per cent of the mineral weighed, and is balanced by iron reduced into the copper button equivalent to .25 per cent of the original sample. On such material it is possible for the assayer, after two months' practice, to tell by inspection the purity of the button within a limit of .1 per cent, either way. The button should have a bright color, and set with a cavity on the upper surface when cooled under the slag without pouring. The surface should be striated.

Low grades (below 40 per cent copper) cannot be visually estimated as closely, but a button entirely free from iron can be distinguished from one carrying enough iron to affect the assay result on 1000-grain samples more than .1 per cent. Such small buttons show no cavity on the upper surface, but should be bright in color and soft under the hammer. Accordingly, low-grade concentrates are fired with less reducer to obtain a pure button, and the copper lost in the slag (.35 to .5 per cent) is quickly estimated with sufficient accuracy by making a rough calculation of the total weight of slag produced, crushing a sample of it, and estimating the copper by the colorimetric test, described in Chapter IV. The total weight of copper slagged is calculated and added to the weight of the button. Check assays on very heavy coarse material should agree within about .5 per cent, on finer grades within .2 to .4 per cent, and on slimes within .2 per cent, including the errors of sampling. From month to month the fire assay results check quite closely the weighed output of the reverberatory furnaces, adding the loss in slag from remelting cupolas.

The electrolytic assay, applied to an equally large sample of at least 60 grams (1000 grains), may furnish accurate results, but it does not include the arsenic present in some Lake copper. For electrolysis, the sample would be dissolved in dilute nitric acid, diluted to one liter, and 100 c.c. of the mixed solution withdrawn for electrolysis. If a residue of coarse gravel remains undissolved, it should be dried, ground, and extracted again.

The fire assay furnishes results in less time, which are well

within the limits of error in daily sampling. Any pimples or purple films on an assay button indicate sulphur, or intrusion of fragments of coal. The color of the slag should vary from dark brown to black with the lower grades.

Furnace. — Assayers employ a rectangular pot furnace, as illustrated in Chapter I, heated by coke and air blast from the smallest commercial size of power blower through a 2.5-inch pipe.

Two rows of fire brick (of 2.5 x 2.5 inches cross-section) are placed across the grate and the fuel is kept at least two inches above the bricks. More fuel is filled in around the crucibles after they have been placed on the cleaned bricks. Different grades from lodes of different formation and tenor in copper require radical changes in the fluxes, especially in the reducing agent. As the heat must be very high, the crucible lining affects the slag. A basic Denver clay crucible, when covered, requires more flux but less reducer than a more open-shaped sand crucible.

Fluxes. — The chemicals must be pure. Sodium bicarbonate is first fused in a large iron ladle without handle, poured into a smooth iron dish to cool, and pulverized through a 20-mesh sieve. Refined borax is melted in a Dixon graphite crucible, poured into an iron dish; and pulverized. Powdered silica and hematite are employed, occasionally, as a corrective, so that the assay slag may contain the average amount of ferrous silicate which experience shows to be the best.

Weighing. — The moist concentrates from the bins (representing the daily tonnage of each grade of mineral) are successively placed on a 15-by-19 inch vulcanite photographic tray which serves as a sampling board. The tray (one side of which is cut out) is slightly moistened with a damp cloth, the sample is coned up, flattened to a layer about an inch thick, and a dip sample of 1000 Troy grains (64.8 grams) taken at nine points by cutting vertical slices with a 10-inch steel spatula. This sample is then mixed on a glazed paper with the weighed fluxes and placed in the marked crucibles. Duplicates are taken of single samples, as also a moisture sample of the same amount, which is placed in a small tin cup and dried on the steam plate. From these data, the percentages of copper may be figured to the dry weights of mineral. Mineral containing 70 to 95 per cent

copper makes so little slag of itself that there would not be enough to cover the button and keep it deoxidized while cooling. Accordingly, a large stock of old assay slag is accumulated, assayed for copper, and a known quantity added to each charge of rich material to act as a cover and regulator. If this assay slag is of average copper tenor, no account is taken of the copper, as it would not add to, or lessen, the weight of the button.

The mineral and fluxes are mixed on the paper, then brushed into the crucibles, and a 3 mm. layer of cream of tartar dusted over each charge. The crucibles are closed with covers made from a mixture of fire clay and ground brick. The coke is filled in around the crucibles, and the blast started. Thousand-grain assays should be melted down to clear fusion in twelve to thirteen minutes, then withdrawn, and uncovered while cooling.

The very coarse "heading" can only be tested with sufficient accuracy by taking several pounds for the original sample,

FLUXES FOR MILL CONCENTRATES OF NATIVE COPPER

Sample	Grade	Per cent copper	Cream tartar	Fused soda carb.	Borax glass	Assay slag	Iron oxide	Fine sand
27000 to 35000.	Heading	90-92	...	1000	400	1000
2000.	Coarse jig	95-90	150	300	150	300
1000.	Fine No. 1-2	65-75	350	150	50	250
1000.	Table slimes, Conglomerate	20-25	300	200	200	0-100
1000.	Amygd., low Fe.	20-40	250	200	200	50-150

Cover. — Cream tartar, in all cases.

drying it in a milk pan to obtain the moisture per cent, then dividing the sample in halves and melting 3 to 5 pounds in Denver K or L Battersea crucibles. To avoid softening and cracking the crucibles with such a heavy charge, the blast should not be used. The fusion may be completed with the natural draft in about one hour. All melts should be withdrawn from the furnace just as soon as they reach quiet fusion, in order to avoid undue reduction of iron into the button. The crucibles should not be jarred while cooling.

The total weight of slag produced from 70 per cent mineral is about 600 grains, and from table (slime) concentrates, about 1200 grains, when a 1000 grain sample is assayed. The proportions of fluxes for different grades are ascertained by experiment. The following table is appended as a basis or starting point, from which the assayer can produce other similar combinations. All weights are given in grains Troy. One gram = 15.432 grains.

PART II

CHAPTER IX

WORK OF THE ELECTROLYTIC REFINERY

SECTION 1. ASSAY OF GOLD AND SILVER BULLION

1. Doré, or Unparted Base Bullion (F. D. Greenwood).

Cupellation in Presence of Gold, Silver, Copper, and Lead. — The sampling has been described on the last page of Chapter II. One gram of Doré is weighed into a piece of lead foil of about six grams' weight, rolled into a cornucopia, and cupeled. The cupel should be "feathered" nicely; cupel to be made of bone-ash, passing through a sieve of 60 meshes to the linear inch (24 per cm.), and to be of medium hardness.

Weigh the tube and place same in test tube, add 10 c.c. nitric acid (1 part HNO_3 (d., 1.42) to 5 parts water). Place test tube in beaker of water and warm until action ceases, then bring water to a boil. Pour off acid and wash with distilled water, then add about 5 c.c. nitric acid (d., 1.42), and place test tube in a beaker of water and boil for one half hour. Pour off acid and wash three times with distilled water. Place the gold in a porcelain crucible, dry, anneal, and weigh.

A proof must be run and treated exactly as the Doré is in each stage, and a surcharge added or subtracted, as the proof loses or gains. A preliminary assay is made of the Doré, and the proof made up accordingly. An assay consists of three Doré weighings and two proofs, cupeled in the following order, and at the same time: 1st, Doré; 2d, proof; 3d, Doré; 4th, proof; 5th, Doré.

2. For Doré containing Antimony. — The gram portion is weighed into a $2\frac{1}{2}$ -inch (6.3 cm.) scorifier with 30 grams of test lead. The proofs are made up according to the preliminary assay. All are scorified in the same muffle at the same time. Pour and hammer the lead buttons into a cube. Should the weight of these lead buttons vary over a gram, make up to

equal weights with sheet test-lead, cupel, and treat exactly as in No. 1.

3. For Doré containing Bismuth, Selenium, and Tellurium.—

Three 1-gram portions are weighed out into a 2.5-inch (6.3 cm.) scorifier with 40 grams of test lead, scorified, and the lead buttons flattened out into a sheet about 3 inches square. This sheet of lead is dissolved in about 200 c.c. of dilute nitric acid (1:3) and boiled to expel red fumes, diluted to 400 c.c., and filtered through three 15 cm. filters folded as one, washing the precipitate only once. Place the three filter papers in a 2.5-inch lead lined scorifier, dry in an oven, burn, then cover with 30 grams of test lead, and scorify. Open the scorification at a rather high heat, continuing with a gradually falling temperature. When the scorifiers have entirely closed over, close the muffle door, raise the heat, and pour; then treat exactly as in method 2. If the silver fineness of the Doré is not three or more times greater than the gold fineness, another set of assays must be run, with the addition of proof silver at the weighing out of the Doré.

MINT ASSAY OF PURE UNPARTED BARS, OR FINE GOLD AND SILVER

4. Assay for Gold.—In all the electrolytic refineries of the United States and Europe the pure material is sampled and assayed practically in the manner prescribed in the respective Mints or Government Assay Offices which purchase the bullion. The assay for fine gold at the Raritan works, for example, varies only in the amount of sample used, duplicate portions of 250 mg. each being weighed out instead of 500 mg., the amount taken at the mints. Dr. Edward Keller's valuable suggestion on the application of copper plate sampling methods to bullion is noted in the last section and page of Chapter II.

A proof of the solubility of gold in nitric acid and a discussion of the conditions affecting the accuracy of the gold assay were presented in two papers by F. P. Dewey.¹ The account of the Mint method has been written up from these papers, from the method of J. B. Eckfelt in the Mint report of 1896, and from the report of Whitehead & Ulke,² including a few personal notes.

Assay.—The Mint sample is usually taken as a triangular chip from top and bottom of diagonally opposite corners of a

¹ *J. Am. Chem. Soc.* **31** (1910), 318. *Trans. A. I. M. E.* **40**, 780 (1909).

² *Eng. and Min. Jour.* 1898, 189.

bar (see Chapter II). The assay balance should be sensitive to .01 mg., and be provided with reading lenses. The chips are flattened, by hammer or hydraulic press, or rolled to a ribbon, marked by stamp with a lot number in such a way that the top can be distinguished from the bottom, and the approximate fineness determined by preliminary assay, or by comparison on the "touch stone" with "needles" of gold of different degrees of fineness. Practice enables an expert to judge within a few thousandths.

To the accurately weighed gold there is added sufficient fine silver, also accurately weighed, to make about twice (or three times, according to another system now less used) the estimated amount of gold in the alloy. (It is customary to make the preliminary assay when the gold contains much base metal.) Extreme care is necessary that the amount of silver added varies as little as possible from the above proportion, as in any marked divergence the result would be liable to inaccuracy. The fact must be emphasized that good results can be obtained with either proportion of silver, because the whole process is comparative, the "proofs" being made up to agree with each set of samples in composition, and carried through under exactly the same conditions. If more silver is used than (2:1), the first acid in parting is made weaker to avoid too violent an action.

The Mints now take for assay 500 mg. of gold, and besides the silver, add about 50 mg. of pure copper if there is none present, as it assists the cupellation, making the resulting button tough on the edges and the final "cornet" smooth. One or two proofs are included with each set of assays of the same kind, to detect inaccuracies and particularly to afford the correction for "surcharge" to be applied to the final results. The assays and proofs having each been inclosed in five grams of lead foil, the assays are ready for the furnace. Some assayers introduce the leads to the hot cupels by a cupel charger, such as that of Keller, which holds forty-eight. T. K. Rose, Chemist of the English Mint,¹ uses a similar apparatus made by Westwood, taking seventy-two at one time, and the cupels are arranged on a plumbago tray which is lifted out of the muffle by an iron peel, the proofs being evenly distributed through the charge. The

¹ *Thirty-fifth Ann. Rep. Eng. Mint*, 1904, 70. *Eng. and Min. Jour.* 80 (1905), 492.

English Mint considers it an improvement to close the space at the back of muffle with fire clay to prevent over-heating; and instead, make an opening in the top, maintaining a separate draft for the muffle.

Cupellation.—After charging the muffle, the door is closed until the leads are melted and the buttons commence to “drive,” when the door is opened until a few minutes before the assays are finished. When agitation ceases and the metal presents a bright surface, the cupels are allowed to cool gradually, and the button of pure gold and silver detached. The exact temperature and time are a matter of experience. The button is brushed clean and weighed, then hammered, annealed, and rolled in small special rolls to a thin strip to furnish a larger surface for the action of the acid. The strips are then coiled around a pencil, or rod, with the stamped end outside.

Parting.—If a few assays are made at a time, as in some refineries, the cornets are parted in crucibles, or test tubes. The Mints use platinum basins of boiling nitric acid, into which are dipped platinum baskets, holding 16 small cups of platinum for the cornets. The first basin contains nitric acid about (1:1), or 22° Beaumé if three parts of silver have been used. If but two parts to one of gold (a former method) are taken, the acid is strengthened to 32° Be. According to F. P. Dewey (*J. Am. Chem. Soc.* 1910, 320), the cornets are now boiled twice in the weaker acid for ten minutes each time, and then in the stronger (3:2) acid for ten minutes. The cornets are then well washed with pure water, transferred to small clay annealing cups, or dried in the platinum cups, and annealed and weighed. The fineness of the gold is expressed in thousandths. By the deviation of the proof, the proper correction is made upon the regular assays, which went through the same furnace charge and were of the same composition.

Platinum.—In an assay of gold containing platinum, the silver must be determined by a wet method, forming a partible alloy by fusion with a diluent metal such as cadmium. The parting operation does not entirely remove the silver, at least, not unless more than three parts of silver were present to one of gold. The “surcharge” of silver, or, exactly speaking, the difference between the firing loss, and gain due to retained silver is very minute, and varies from two to seven or eight ten-

thousandths. According to Whitehead, duplicates should agree within .2 or .3 of a part except in the case of very base bullion.

In assaying fine (or nearly fine) gold, the proof is weighed to 1000 parts of test gold; but in testing ingots for coinage, etc., a proof of 900 parts is used, and in lower grades a synthetic proof is made up to correspond, as already explained. Duplicate assays serve also to show if the gold bars are of uniform fineness throughout. If the assays show undue variation, the mass from which the sample was taken is remelted and stirred (after Mint methods), then cast and assayed in duplicate as before. It is often expedient, with low-grade gold, to add sufficient fine gold (as in Doré methods), in order that the assay may contain 900 parts of gold in 1000. In this way the exact fineness of the alloy is ascertained, otherwise a slight allowance would have to be made for the cupel loss, which will happen when a large proportion of alloy is present. When the weight of cornet is obtained, the weight of fine gold which was added, must be deducted, the difference being the fineness of the original alloy.

Sometimes the ordinary amount of lead is insufficient to completely eliminate all the base metals, or the cupel may not be able to absorb all the lead which such an assay would require. In such cases it is accordingly customary to weigh the assay at one-half the usual weight, adding fine gold sufficient to render the mixture 900 fine, and then adding enough silver to secure the right proportion of the latter to the gold. Some chemists use a system of "gold weights" in which 1000 parts equals .5 gram.

5. Preparation of Pure Gold.—Refineries may obtain their proof gold directly from the Governments. Such metal can be prepared by the method of McCaughey¹ and Eckfeldt. Proof gold at the Philadelphia Mint was made from electrolytic of 999 fineness. The latter was dissolved in aqua-regia and allowed to stand for two weeks. The solution was decanted from any silver chloride, and potassium chloride and alcohol added to precipitate any platinum. After standing two weeks, the solution was decanted and precipitated with sulphur dioxide. The gold was redissolved, the above steps repeated, and the final

¹ *J. Am. Chem. Soc.* **31**, 1262.

precipitation made with oxalic acid. The separated gold was melted in Beaufay crucibles under borax, and rolled into ribbons .009 inch thick. From this ribbon, little pieces were taken and washed with alcohol. F. P. Dewey quotes the same method.

FINENESS OF SILVER BULLION

Limitation of Methods.—The cupellation method, used for gold, gives such uncertain results for silver in high-grade bullion that it is now used in a subsidiary way for approximate results (Eckfeldt). The “wet” or humid assay of Gay Lussac, with proper care and attention, may be regarded as a perfect process, if performed by an expert operator. Some refineries employ a combination method which is more convenient.

6. The Humid Silver Assay (F. P. Dewey).¹—1115 mg. of standard metal (generally about 900 fine to 1000 parts) is weighed and transferred to a glass-stoppered bottle, the metal dissolved in nitric acid, and 100 c.c. of a standard solution of sodium chloride run in. The bottle is then vigorously shaken and a measured portion of a decimal salt solution added, and again shaken, if necessary. These operations are repeated until the silver is precipitated. If standard (900 fine) silver is to be tested, 1115 mg. should carry 1003.5 mg. of silver, a convenient figure. The variation of such metal in actual silver present above or below 1003.5 mg. is not excessive. For testing the standard salt solution, 1004 mg. of proof silver is weighed and single weights are used of 1115 and 1004 mg.

(In some copper refineries the metal to be valued is the fine bullion produced by parting and refining the Doré and with such pure metal about 1004 mg. would be taken.)

The bottles should be of perfectly white glass, carefully made and well annealed; 8 ounces (250 c.c.) is a convenient size often used; the bottles are most conveniently handled in a circular frame or basket holding ten. For dissolving the silver, both the amount and strength of nitric acid may vary considerably without apparent effect upon the accuracy of the results, 8 c.c. at 1.30 sp. gr. to 25 c.c. at 1.20 sp. gr. being allowable. Some operators heat the bottle to remove nitrous fumes, others do not. The standard salt solution is designed to have 100 c.c. precipitate exactly 1 gram or 1000 mg. of silver, but it seldom

¹ *Bull. A. I. M. E.* **76** (1913), 587.

"shows" this exact strength. The word "shows" is used instead of "is" because the equivalent of the solution depends on other factors besides its composition. In general, two proofs should be used in every set of ten bottles, unless several tests are run in rapid succession, when one proof in each set may answer. Some operators run an independent proof occasionally during the day and omit the proof in the sets, but this proceeding is objectionable.

The next step in the method is the addition of 100 c.c. of the standard salt solution (improperly termed normal). This is a very simple operation, but it requires the utmost care and attention to details if high accuracy is desired. Even a minute variation in the addition will make a serious variation in the fineness of silver shown.

The Stas pipette is the one universally used in the Mints. It is a simple pipette open at both ends and securely mounted on a wall bracket. The upper end is drawn out to a fine opening and is provided with a collar-cup to catch the drip. The lower end is comparatively large and must have a free and smooth discharge. The lower end is connected, by means of a removable rubber tube provided with a pinch cock, with an elevated tank containing the salt solution. No stop cocks, floats, or graduations of any kind can be used on or in the pipette if rapid work is to be done.

In operation, the rubber tubing is slipped over the lower end and the pinch cock opened. As soon as the solution comes out of the upper end of the tube, it is closed by the first finger of the left hand and the cock closed. The operator must now be sure that there are no air bubbles in the pipette. If such should appear they must be allowed to collect at the top of the pipette; the pinch cock must be opened, the finger momentarily removed from the upper end of the pipette, and the pinch cock closed again. When the pipette is full of solution and the pinch cock closed, the rubber tube is withdrawn from the lower end of the pipette. This end must now be carefully examined to see that there is no surplus solution adhering to it or that the air has not commenced to ascend the tube.

If the lower end of the tube is in proper condition, the silver bottle is now placed directly under it, the finger removed from the upper end, and the solution allowed to flow out rapidly in a

smooth solid stream. Just as soon as the flow stops, the bottle must be removed. It is absolutely fatal to accuracy to attempt any adjustment of the drip of the pipette. There should be only just easy clearance between the bottom of the pipette and the top of the bottle. The pipette is supposed to contain 100 c.c. and it is desirable that it should be fairly accurate, but, absolute accuracy is not necessary. The absolutely essential point about it is that it should deliver exactly the same amount of solution to each one of the ten bottles in a set. The amount may not be quite 100 c.c., or may vary slightly from summer to winter, but it should not vary from the first to the last bottle in a set. It is a good plan to fill and empty the pipette a few times before filling the set. After withdrawing the bottle from under the pipette, the stopper is dipped in distilled water and inserted in the neck of the bottle with care. Having filled the set, the carefully stoppered bottles are placed in a shaker and agitated from three to five minutes to settle the precipitate. The bottles are next placed on a black shelf, technically called "a board," with a black background about as high as the shoulder of the bottle and about three inches in the rear, the whole being installed in a window, preferably with a northern exposure.

Modifications. — Beyond this point there are slight differences in the manipulation in different laboratories. In common with many volumetric methods, there is difficulty in determining the end-point. The assays are finished with a "decimal solution," 1 c.c. of which neutralizes 1 mg. of silver. In many descriptions the operator is directed to add decimal salt in small amounts, with agitation between the additions, until no more precipitate is formed by further addition. Too much salt has now been added, and this excess must be determined by the addition of small amounts of decimal silver solution, and the amount of silver present in the metal determined by balancing these amounts. This method is open to two serious objections. When exactly the proper amount of salt has been added to throw out all of the silver present, equilibrium results, which is disturbed by the addition of either reagent with the separation of a precipitate. This obscures the end-reaction. These alternate closings and shakings consume too much time for rapid work, and after repetitions, the solution does not clear well.

In the Mint service, therefore, operators "read the cloud" instead of repeatedly dosing the solution. This operation is far more rapid, but requires a great deal of skill and constant practice to yield the best results. In reading the cloud, after the addition of 100 c.c. of standard salt solution and shaking, a measured amount of 1 or .5 c.c. of decimal salt solution is added to each bottle. The delivery end of the pipette is placed against the neck of the bottle as far down as possible and the solution allowed to flow gently down the side so that it will remain on the surface of the solution with the minimum amount of mixing; by a slight rotary motion of the hand the decimal solution is then mixed with the upper portion (about one-third) of the bottle solution. This produces a cloud of silver chloride in the solution, and the next step is based on the appearance of this cloud. Here the skill and visual condition, together with the personal equation, of the operator are of the utmost importance.

If the cloud be very heavy, two or more portions of the decimal salt are added, the amount depending on the density of the cloud, and the bottles shaken in the machine again. If the cloud is light, only one dose of decimal is used, and the bottle is again shaken by hand to bring more of the solution into reaction and again examined. As the result of this treatment, one dose of decimal may be used, or the bottle may be shaken by hand again to bring the balance of supernatant solution into reaction. Here again a dose of decimal solution may be used or the final reading of the cloud may take place. In the final reading the operator estimates from the density of the cloud what portion of the dose of decimal solution was used up in precipitating the silver. Many operators estimate to .25 c.c., others claim to be able to estimate to .1 c.c., but Mr. Dewey's figures indicate that reading to .1 c.c. on standard (900) metal is not profitable (*loc. cit.*).

All of the bottles are eventually brought down to the final cloud, and at the end the amount of decimal solution added to each bottle is recorded. The records of the assays are then compared with the proofs and the fineness of the samples determined. The actual fineness is shown entirely by the amount of decimal solution as compared with the amount of decimal required by the proof. It is entirely independent of the amount of standard solution used. Therefore, in determining the fine-

ness of a sample we simply compare the amount of decimal used with that in the proof, making allowance for the .5 mg. additional silver in the proof above the silver in 1115 mg. of metal at the exact standard of 900, and taking into consideration the weight of sample used. For instance, if the sample required .5 c.c. less than the proof, the sample would be reported at 900. This is not strictly exact because .25 c.c. of decimal salt solution equals .25 mg. of silver, but .25 mg. is only .22 fine on 1115 mg. and .5 would be only .44 fine. In general, however, the finenesses are read directly from the difference between the sample and the proof, and in .25 of a cubic centimeter. Practically one-half is deducted from the amount of "decimal" used on the proof and it is called standard (900). Then for each quarter's difference for standard the assayer adds or subtracts from each 900 according to this tabulation:

For $\frac{1}{4}$	0.2	For $\frac{6}{4}$	1.3
" $\frac{2}{4}$	0.4	" $\frac{7}{4}$	1.5
" $\frac{3}{4}$	0.7	" $\frac{8}{4}$	1.8
" $\frac{4}{4}$	0.9	" $\frac{9}{4}$	2.0
" $\frac{5}{4}$	1.1	" $\frac{10}{4}$	2.2

A second method of determining the end-point, which appears to be even more exact but requires more time, consists in adding only .25 c.c. of the decimal solution after machine shaking, then estimating the number of quarters the solution will stand. These are added and the bottles shaken in the machine. This is continued until the quarter added after shaking produces no precipitate, in which case the last quarter is not counted, or else such a slight precipitate is produced that the quarter is counted but the bottle is not shaken again. The reading of the results is the same as before described. In both these methods great care is exercised to avoid the addition of so much salt as to require any reverse titration with silver solution.

7. Titration of Silver in Bullion.—Owing to the fact that constant practice is required to enable the operator to check by the original Mint method within 1 fine on a sample of silver bullion, the following titration, devised by F. Andrews, is better adapted to the work of electrolytic refineries. This method of titration is a modification of the original one attributed to Volhard¹ or Charpentier.²

¹ *J. Pract. Chem.* 1874.

² *Compt. Rend.* 1871.

Weigh out 2 grams of fine clean drillings, or granulations, and 2 grams of 1000 fine proof silver (standardized by U. S. Mint or Assay Office) into 200 c.c. graduated flasks with long necks. Dissolve in 35 c.c. of (1 : 2) nitric acid, boil off red fumes, and cool to room temperature. In all the subsequent operations the standards must be treated just like the bullion. Run in without draining, by an automatic pipette 100 c.c. of a standard solution of hydrochloric acid of such strength that 100 c.c. precipitates a few milligrams less than 2000 mg. of silver. Cork the flask with a rubber stopper and shake until the solution is clear. Wash off the stopper and neck of the flask and make up to the 200 c.c. mark; cork the flask again with a dry rubber stopper and shake well to mix the contents. If the flask is not of a design to permit mixing by shaking, pour the contents three times into a dry beaker. Let the silver chloride settle for one hour and then measure off 100 c.c. of clear solution by means of a measuring tube into an Erlenmeyer flask. Add 3 c.c. of a saturated solution of iron alum as an indicator and titrate with a standard solution of ammonium thiocyanate. 1 c.c. of the thiocyanate finishing solution equals .001 gram of silver; the end-point is a reddish brown. A comparison of the quantity of reagent used in titrating the sample and the proof determines the fineness.

7a. Second Modification¹ (F. P. Dewey).— Impure auriferous bullions are titrated with thiocyanate alone, finishing with decimal strength. Wrap .5 gram in 1 g. lead foil and fuse under potassium cyanide in a scorifier with 10 parts of cadmium. Boil in 60 g. of 32° nitric acid and dilute with 100 c.c. water before adding the indicator. Silver chloride reacts slowly and mercury or palladium interfere. Moderate amounts of copper and platinum do not. Cobalt and nickel obscure the end-point, but the back-titration may be employed. Ferrous iron and nitrous oxide must be absent.

SECTION 2A. THE CONTROL OF ELECTROLYTES AND ANODE SLIMES IN THE ELECTROLYTIC REFINERY

8. Free Sulphuric Acid in the Electrolyte.— The vat solution is conveniently delivered to the laboratory in large glass-

¹ *J. Ind. and Eng. Chem.* **6** (1914), 650, 728; Abstract, *Eng. and Min. Jour.* **99**, 355.

capped jars, is cooled to room temperature, and the specific gravity (or density) taken with the hydrometer. All large refineries use practically the same method. (Most of the description is due to J. Klein.) The solutions required are:

(a) *Normal Solution of Sulphuric Acid*.—49.04 grams H_2SO_4 , or its equivalent of pure (93 per cent) acid, is dissolved in 500 c.c. of distilled water, cooled and diluted to 1000 c.c. at 70° Fahr. with distilled water. This is first standardized against sodium carbonate.

(b) *Normal Sodium Carbonate*.—26.5 grams of anhydrous chemically pure sodium carbonate is dissolved in distilled water at 70° Fahr. and diluted to 500 c.c. The indicator is made by dissolving .05 gram of dimethylamidoazobenzol (methyl orange) in 75 c.c. of 95 per cent alcohol. The normal solution of sulphuric acid is also valued by measuring out a definite amount, say 20 c.c., adding a little hydrochloric acid, and precipitating with barium chloride, then weighing the filtered and ignited sulphate of barium. This serves as a check.

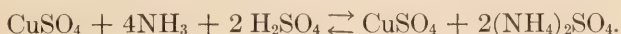
(c) *Standard Potassium Hydroxide*.—Thirty (or sixty) grams of Merck's purified sticks are dissolved in water and diluted to 1000 c.c. and standardized against the sulphuric acid when made.

(d) *Standard Solution of Copper Electrolyte*.—100 grams of pure copper sulphate crystals and 147 grams of sulphuric acid (d., 1.835) are dissolved in 500 c.c. of water, cooled, and diluted to 1000 c.c. This is standardized by precipitating the copper from a measured amount by electrolysis and calculating the value in copper. Solution is kept in stock and used to standardize both the potassium hydroxide and cyanide.

Determination.—Take two 5 c.c. portions of the sample of electrolyte, add 20 c.c. of water and 3 to 8 drops of indicator, and titrate with the standard solution of potassium hydroxide, and then calculate the amount of free acid in grams per liter. By dividing the result by the specific gravity, the percentage of acid by weight is easily obtained.

9. The Mansfeld Process of Titration.—H. Koch has modified the old method of Kieffer to make its titer definite. The titrating solution is made by dissolving a known weight of the complex cupric-ammonium sulphate in water. The process depends on the double decomposition which this salt undergoes

by the action of free acid, the latter uniting with the ammonia, setting free ammonium sulphate and cupric sulphate, both of which dissolve clear in the fluid.



On saturation by free acid, the ammonium in the complex salt goes to the acid radical in the CuSO_4 and precipitates copper hydroxide. As a sign of the end-reaction, there occurs, with the slightest excess, a distinct turbidity of the liquid. The titer is not empirical but systematic; the quantity weighed is determined by the formula of the hydrated complex, $\text{CuO}, \text{SO}_3(\text{NH}_3)_4.(\text{OH})_4$. Dividing the molecular weight by 2 gives 122.72 parts. If two molecules of sulphuric acid exactly neutralize one molecule of cupric ammonium salt, the weight of the standard "salt" to be taken is $\frac{122.72}{2}$ or 61.36 grams per liter. Actually the standard solution of commercial salt requires 65 grams on account of its moisture. An improvement is also effected by the addition of 6 grams of ammonium sulphate. The fluid then remains clear for a month and its titer unaltered, provided that good uncrushed crystals of the complex salt are employed.

The two weighed salts are dissolved in about 800 c.c. of cold water, filtered, and diluted to one liter with the distilled water after standing for twelve hours. The water must be freed from carbon dioxide before use by long boiling. The addition of the ammonium sulphate, as recommended, exercises no subsequent influence on the solubility of the cupric oxide, so that the results of titrations for free acid performed under varying conditions check very closely. Method 8 is preferred in the United States, as the end-point is so distinct, and the normal alkali may be more accurately standardized.

COPPER IN ELECTROLYTES

10. Titration by Potassium Cyanide. — The time which may be allowed for a test and the percentage of impurity in the electrolyte will naturally govern the choice of methods from those to be described.

Cyanide. — As much as 60 grams per liter have been used, but the writer prefers a solution of 24.5 grams of 98 per cent salt, or 24 grams of pure salt, per liter.

This solution may be standardized against the standard electrolyte, or against a solution made by dissolving .2 gram of 99.95 per cent copper in pure nitric acid (d., 1.2). Evaporate to dryness, dissolve in water, add 10 c.c. of strong ammonia, cool, and titrate with cyanide, then calculate its value in copper. The titration of this standard should be made in the same time and conditions as the tests of works samples.

Vat Solutions. — Take two 5 c.c. portions of the electrolyte, add 20 c.c. of water, 5 c.c. of nitric acid, and heat nearly to boiling to oxidize ferrous iron, etc. Now add 10 c.c. of ammonia (d., .9), cool to room temperature, and titrate with cyanide, observing the same rules as in standardization. Occasionally check by electrolysis.

11. Titration by Potassium Permanganate for Copper. — R. Cobeldick precipitates copper as thiocyanate and then redissolves and titrates.

1 c.c. of electrolyte is run into a 150 c.c. beaker, diluted to 100 c.c., heated to boiling, and treated with 10 to 15 c.c. of sodium sulphite (200 grams per liter), then with 5 to 10 c.c. of potassium thiocyanate solution (40 grams per liter). The liquid is boiled for two minutes, allowed to stand for ten minutes, filtered, the filter washed four times with hot water, and the contents decomposed with hot 8 per cent sodium hydroxide. The copper precipitate is washed well with hot water, the solution made acid with sulphuric acid, boiled, and titrated with standard potassium permanganate (1 c.c. = .002 gram of copper). The copper value $\times 4$ = the blue vitriol ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). The objection to this scheme is the manipulation, and the small sample treated, but the principle of separation is valuable for impure electrolytes.

12. Mansfeld Method of Titration with Sodium Sulphide. — In order to render the end-point distinct, the solution is shaken during titration with a large quantity of chloroform, or better, carbon tetrachloride. It is necessary to keep the copper within certain limits. If copper solutions are too rich, the results are uncertain, hence the solutions must be divided so that not over 50 c.c. of sulphide are used. If a works sample is to be tested, 25 c.c. are diluted to 250 c.c., from which 25 c.c. (2.5-gram samples) are withdrawn for titration. The conditions of dilution and acidification should be followed exactly as described.

The test liquid is placed in a stoppered flask of about 300 c.c. capacity, 20 c.c. of (25 Be.) sulphuric acid added, diluted with water until the flask is half full, and finally 60 c.c. of carbon tetrachloride poured in. Some standard sodium sulphide is allowed to flow in, the flask stoppered and shaken vigorously. The supernatant liquid becomes water-clear. The shaking is repeated with each addition of sulphide, until the last addition causes only the slightest turbidity. The clarification proceeds slowly with old solution, containing thiosulphate formed by oxidation. So it is recommended that illuminating gas be kept in the bottle above the solution, charging the solution through the lower tubulure of the stock bottle.

The sodium sulphide is prepared as an approximately normal solution. The requisite sodium hydroxide is first dissolved in 500 c.c. of water, then divided in two equal parts, and one-half saturated with hydrogen sulphide. The other half is now added and the whole diluted to one liter. The solution is standardized against pure copper. The process is also used, in Germany, for lean slags or ores of lead, but is not favored in the United States.

13. Copper in Vat Solution by Electrolysis.—Instead of dissolving and titrating sulphocyanate of copper F. D. Greenwood redissolves and electrolyzes the precipitate. 10 to 20 c.c. of electrolyte are treated as in **11**, the white salt filtered, washed, dissolved in acid as described in Chapter X, method 4, and the solution electrolyzed for copper.

CHLORINE IN ELECTROLYTES

14. Combination Method.—According to J. Klein, 500 c.c. of electrolyte should be treated with 40 c.c. of nitric acid (d., 1.42), stirred, and allowed to oxidize. Then add 1 c.c. of a normal solution of silver nitrate, allow to stand in a warm place for forty-eight hours, filter, cupel the silver chloride, and calculate the chlorine by multiplying the weight of silver by the factor .32858. Instead of cupeling, the chloride may be filtered from solution on an asbestos felt, which has been extracted with nitric acid, dried, and weighed before use. The silver chloride is finally dried at 130° C. and weighed as chloride. In order to weigh directly, the original electrolyte should be clear and free from all suspended sediment.

DETERMINATION OF OTHER IMPURITIES

15. Separation of Copper and Antimony from other Metals.

— To 10 c.c. of electrolyte add 200 c.c. of water and 15 c.c. of sulphuric acid (d., 1.835), pass hydrogen sulphide to precipitate metals, and when the reaction is complete, filter, wash well with hot water, and place the filtrate on the hot plate to evaporate for the determination of iron, aluminum, nickel, and cobalt. The following method is the one adopted by J. Klein, with some modifications by the author.

Transfer the sulphides to a beaker and digest with 15 c.c. of a saturated solution of sodium monosulphide diluted with 100 c.c. of water. Heat to 150° Fahr. for about an hour, filter while hot, and wash well with hot water containing a little hydrogen sulphide. The paper with precipitate is transferred to the beaker in which the hydrogen sulphide treatment was performed, treated with 100 c.c. of nitric acid (d., 1.2), and placed on the steam plate until all copper is dissolved. Do not heat too high, as the filter paper will become too fine and retard the filtration. Filter and wash well. To the filtrate add 5 c.c. of pure sulphuric acid (d., 1.84), evaporate to fumes, dilute, add 1 c.c. of nitric acid, and electrolyze for copper, if a check is desirable on the cyanide titration.

Antimony. — The sodium sulphide extract is treated with an excess of dilute sulphuric acid, the arsenic and antimony filtered off, and separated by digestion with hydrochloric acid (d., 1.16). Filter off the arsenious sulphide, wash well, add about 1 gram of sodium chloride and 2 grams of tartaric acid, evaporate to about 50 c.c. to expel hydrochloric acid, and dilute with water to 200 c.c. Pass hydrogen sulphide, allow to settle, filter off the sulphide of antimony, and dissolve it in ammonium sulphide by digesting the filter with the reagent, or by dropping some around the filter and then treating with hot strong ammonia. Evaporate to a small bulk, acidify with nitric acid, evaporate, add nitric again, transfer to a small weighed porcelain crucible, evaporate twice with nitric acid, heat the residue, and weigh as antimony tetroxide.

16. Iron, Aluminum, Cobalt, and Nickel. — The filtrate from the hydrogen sulphide separation is evaporated to drive off the hy-

drogen sulphide. When the volume has been reduced to 100 c.c., add 50 c.c. of strong hydrogen peroxide and evaporate to white fumes, cool, add 50 c.c. of water and evaporate to white fumes again, repeat the operation, and then dissolve in water. Make the solution slightly alkaline with ammonia, boil, and filter off the alumina and ferric hydroxide. Finally, wash, dry, ignite and weigh the precipitate, and calculate its amount in grams per liter. Evaporate the filtrate from the iron to 100 c.c., render it strongly ammoniacal, and precipitate the nickel and cobalt together on weighed platinum electrodes, with a current density of .75 to 1 ampere. A strong solution of sodium sulphide may be used to test the completeness of the precipitation.

Titration of the Iron.—Fuse the weighed precipitate of alumina, etc., with sodium carbonate, treat the fused mass with hot water, make the liquid acid with sulphuric acid, reduce the iron by any reliable method, and titrate with standard potassium permanganate. (See Chapter V.)

(b) *Alternative Method for Nickel.*—The copper and other similar metals are removed by hydrogen sulphide, as in the previous treatment (15). Boil the filtered solution in a flask for ten to twenty minutes with 5 c.c. of a mixture of bromine and hydrochloric acid, then add 5 c.c. of nitric acid and boil one minute longer. Cool the solution, add an excess of ammonia, filter into a No. 2 beaker, and wash the ferric hydroxide thoroughly with hot water. Add 10 c.c. of saturated ammonium carbonate solution to the filtrate and electrolyze for nickel with a low current of only .1 to .15 ampere per square decimeter of immersed cathode surface. This modification is due to Cobeldick.

17. Arsenic in Electrolyte.—Place 5 to 25 c.c. of electrolyte in a 300 c.c. Erlenmeyer flask, which is connected to a vertical 8-inch Allihn glass condenser by a glass tube which has a slight rise of one inch after leaving the flask. (See Fig. 14, Chapter XII.) The flask is mounted on a thin plate heated by gas or electricity. Add to the flask 2 grams of ferrous chloride, or sulphate, and close the flask with the rubber stopper.

Pour through a 60 c.c. separatory funnel 10 c.c. of sulphuric acid (d., 1.84), then follow with 50 c.c. of hydrochloric acid (d., 1.16), and distill to about 25 c.c. volume. Add 30 c.c. of hydrochloric acid, 1 c.c. of a 10 per cent solution of hypophos-

phorous acid, and distill down to 25 c.c. again. Repeat the same addition and distillation, when the arsenic should all be in the distillate. To prevent the distillate sucking back into the flask, the bottom of the condenser should be kept just far enough below the surface of water in the receiver to effect a seal for the vapors evolved. Make the total distillate alkaline with ammonia, then just acid with dilute sulphuric acid, using litmus paper as an indicator. Cool in a basin of water to room temperature and make alkaline with ten grams of sodium bicarbonate, or use a considerable excess of a saturated solution of the same salt.

The volume of the solution is now about 400 to 500 c.c. Pour off about 100 c.c. of this solution into a graduate (if rich in arsenic). Titrate the whole or the aliquot portion with a standard solution of iodine and potassium iodide. 1 c.c. equals .001 gram of arsenic (21, Chapter III).

A hydrochloric acid made by the electrolytic process is the best suited to such work.

ANALYSIS OF ANODE MUD, OR SLIMES

Preparation. — Electrolytic slimes, as received, are washed free from all soluble sulphates, then dried and ground to pass a screen of 60 meshes to the linear inch. The next four methods are due to Klein.

18. Determination of Arsenic. — Weigh 1 gram of dried sample, dissolve in nitric acid, add 15 c.c. of sulphuric acid, evaporate to white fumes, cool, add 50 c.c. of water, repeat the evaporation to fumes twice, then transfer to the distilling flask, and distill exactly as in the preceding method (17). Titrate the arsenic.

19. Gold and Silver in Boiled Slimes from Lake Copper. — Place 5 grams of test lead on a cupel, weigh out .2 gram of sample and place it on the cupel, add 5 grams more of test lead, mix, cover with test lead, cupel directly, and weigh the button.

(b) *Silver in (Lake) Raw Slimes.* — Place 15 grams of test lead in a 3.2 cm. ($2\frac{1}{4}$ inch) scorifier, weigh out .5 gram of the slime, place it in the scorifier, add 15 grams more lead, mix the charge, cover with test lead, add a little litharge and borax glass, and scorify. If the button of lead is too hard, rescorify with the addition of test lead and a little borax; cupel and weigh the resulting silver button.

20. Silver in Slimes from Converter Copper. — According to Greenwood, these slimes are assayed by the same method as given for Doré bullion containing bismuth, selenium, and tellurium, except that no proof is run, or correction made on slag and cupel.

21. Insoluble Matter. — Weigh out 1 to 2 grams of dried slimes, dissolve in nitric acid, and filter the extract. At some works, it is customary to determine the *chlorides* in this material.

Fuse with a mixture of equal parts of sodium carbonate and sulphur, dissolve the fusion in water, filter, and wash. Heat the residue to boiling, with nitric acid (d., 1.2), dilute and precipitate the silver with hydrochloric acid. Stir, heat, and decant through a filter, keeping the silver in the beaker. Then add hot water and a few drops of hydrochloric acid, boil, decant through the filter, repeat the operation, and discard the silver chloride.

22. Lead. — Evaporate the filtrate to 100 c.c. Filter off and discard any silver chloride which may appear at this time. Make the solution alkaline with sodium hydroxide and add the solution of the sodium carbonate-sulphur fusion in order to precipitate all the sulphides of the copper group. Digest, heat to boiling, filter, and reserve the filtrate for the determination of antimony and tin (26). Place the precipitate in the beaker, dissolve it in nitric acid (d., 1.2), wash well, add to the filtrate 10 c.c. of sulphuric acid and evaporate to white fumes. Cool, add water, and repeat the evaporation twice. Add water and alcohol and filter off lead sulphate and insolubles. Digest the mass with ammonium acetate to dissolve the lead sulphate, filter, and wash; then add an excess of sulphuric acid to the extract to precipitate the sulphate of lead. Filter on a weighed porcelain Gooch crucible, ignite carefully, and weigh.

23. Copper Assay. — In complete analysis, boil down the filtrate from the lead, neutralize with ammonia, then make acid with 3 c.c. of sulphuric and 2 c.c. of nitric and electrolyze for copper.

Copper may be estimated directly in an original solution of a 2-gram sample of the slimes, if interfering elements are first removed. This may be effected by the addition of sodium sulphite and thiocyanate, or by repeated precipitation with excess of ammonia after adding 6 grams of ferric alum. In the former

case the white salt of copper is decomposed with nitric acid. Electrolyze or titrate as directed for ores in Chapter IV.

24. Cobalt and Nickel. — Instead of dissolving the original slime sample in nitric acid, it may be digested two to three hours with aqua-regia if preferred (Cobeldick). Evaporate to dryness with excess of sulphuric acid and heat to white fumes to expel all the hydrochloric acid. Take up the dry mass with water and a little sulphuric acid, warm until all soluble matter is dissolved, and filter into a 250 c.c. beaker. (If the solution was so impure that it was found necessary to separate the copper first as thiocyanate, the excess of reagent should be destroyed before any attempt is made to estimate cobalt and nickel, the arsenic and selenium being removed as sulphides — **22**.)

Determine copper by electrolysis and separate lead as already described. Evaporate the filtrate or electrolyte and washings to fumes if any nitric acid is present in the assay. About 5 c.c. of sulphuric acid should now be present, unless the carbonate modification is adopted.

Nickel and cobalt are then obtained from the solution. Boil with an excess of ammonia, filter off the ferric hydroxide, and estimate the iron by weighing the ignited oxide, or by titration with permanganate.

Treat the filtrate from the iron with 20 c.c. of strong ammonia, or with 15 c.c. of a saturated solution of ammonium carbonate, and electrolyze. With sulphate use .5 ampere per sq. decimeter. With a carbonate solution, the current should be no more than .10 to .15 ampere. Total volume 100 c.c.

25. Antimony and Arsenic in Slimes. — To the alkaline filtrate from the soda-sulphur fusion (**21**) add sulphuric or acetic acid to precipitate the arsenic, tin, and antimony. After settling, filter, wash, dissolve in ammonium sulphide, and evaporate to dryness on the steam plate. Separate the tin, preferably, by the method of G. W. Thompson, as described in full in the analysis of copper, Chapter XIII. The residue is boiled with equal parts of ammonium oxalate and oxalic acid solution and treated with hydrogen sulphide. The precipitate is filtered off and the filtrate reserved. The sulphides of arsenic and antimony are then separated by digestion with hydrochloric acid (1.16), the antimony oxidized, ignited in porcelain, and weighed as the tetroxide.

26. Tin is separated from the oxalic acid by evaporation to fumes with sulphuric acid, after which the diluted solution is neutralized with ammonia, acidified with acetic, and the tin thrown down by hydrogen sulphide.

Allow to settle, filter off the tin sulphide, wash well, place the paper and contents in a beaker, add nitric acid (d., 1.2), evaporate, repeat this operation a second and third time, or until the tin is completely oxidized. Filter on a porcelain Gooch crucible fitted with an asbestos felt, ignite, and weigh as stannic oxide, SnO_2 . Traces of selenium will be mostly volatilized.

27. Alternative Method for Insoluble Matter.—Take a 1-gram sample and dissolve in nitric acid, then filter, wash, and treat the residue with a boiling solution of ammonium acetate until the lead sulphate is extracted. Dry the residue and carefully ignite it in a platinum crucible, after which it may be weighed, if desired.

Fuse the residue with sodium carbonate and potassium nitrate in equal parts, dissolve in water, transfer to a casserole, add hydrochloric acid, and evaporate to dryness below 110°C . Cool the residue, and repeat the addition of acid and evaporation a second and third time. Finally, take up with 100 c.c. of water and 20 c.c. of hydrochloric acid, boil, filter, wash the residue thoroughly, ignite, and weigh.

28. Sulphur in Slimes.—Dissolve 1 gram of slimes in nitric acid, boil, dilute the solution, filter on a paper filter, and wash the residue. Place the filtrate on a hot plate, add hydrochloric acid in sufficient amount to precipitate all the silver, stir well, filter, and wash the paper, discarding the silver chloride. Evaporate the filtrate, reserve any insoluble residue, and fuse it with the mixture of sodium and potassium carbonate. Transfer the fusion to a casserole and dissolve it in water, add hydrochloric acid carefully in excess, evaporate nearly to dryness, dilute, heat to boiling, and filter, adding this filtrate to the first filtrate. Evaporate the whole to dryness, and if any silver chloride appears on dilution, filter it off and discard. Evaporate twice to dryness with dilute (1:2) hydrochloric acid, dissolve in the same acid, filter, heat to boiling, and add barium chloride. Settle, filter, wash, ignite, and weigh the sulphate.

29. Platinum and Palladium.—Some slimes contain traces of these valuable metals. They may be separated from gold

and silver by dissolving in sulphuric acid, filtering and melting the residue by crucible fusion, and following the same methods adopted for ores (8, 9, 10, Chapter VIII).

Selenium and tellurium may be precipitated from a sulphuric acid solution by method 7, Chapter XII.

SILVER REFINERY SLAGS

30. From Bullion Refining Furnace. — The sample received may consist of several pounds of coarsely crushed slag which has been reduced from a larger sample in the electrolytic department by means of rolls or gyratory mill. Reduce the slag to pass a sieve of 60 meshes to the linear inch (24 per cm.), weigh the whole, and also weigh and separately assay the pellets remaining on the sieves. Dissolve the pellets, or a weighed portion, in dilute nitric acid, filter off the residue for gold assay, then determine silver by wet method and copper by color test.

Assay of the Fines for Silver and Gold. — A portion of 3 to 6 grams (.1 to .2 A. T.) of the fines may be melted in a crucible with about 40 grams of litharge, 30 grams sodium carbonate, 10 grams of borax, and 1.5 grams of flour. After pouring, the slag is re-melted in the same crucible with a little soda and 1 gram of flour. Cupel the two lead buttons together.

For greater accuracy, the large lead button should be cupeled first and the cupel melted up with the second crucible fusion. If preferred, the fines may be directly scorified with sufficient lead and .5 gram of borax.

Assay for Copper. — Weigh 2 grams of fines and boil in a 100 c.c. platinum dish or a four-inch casserole with the following mixture: 15 c.c. sulphuric acid, 6 grams potassium bisulphate, 5 c.c. nitric acid, and about 5 c.c. hydrofluoric acid. The latter should be added quickly and mixed by rotation. The solution should be evaporated to dryness, heated to fuming for half an hour, and, if the residue is not white, treated with 5 c.c. of sulphuric acid and 5 c.c. hydrofluoric acid and boiled until the nickel oxide is dissolved. Dilute and precipitate the silver; then filter.

Determine copper by method 23. Other impurities are also estimated by the methods for slimes.

CHAPTER X

THE ELECTROLYTIC REFINERY

VALUATION OF BLISTER, CONVERTER SLABS, AND ANODES

GOLD AND SILVER

Preparation and Weighing of Samples. — The sampling of crude metal at the furnaces, or in carloads at custom works, has been described in Chapter II. The final subdivision of the sample in the laboratory to the assay weight is, however, equally important. There is some difference of opinion as to the necessity of sifting variable material before division into "coarse" and "fines" to be separately assayed. From written opinions and personal experience, it is evident that the manner in which samples are cut to final assay weight depends on the character of the material treated in each laboratory.

If the material is very variable or non-homogeneous, the sample of 4 to 5 pounds (1.8 to 2.2 kg.) is ground to pass a $\frac{1}{16}$ -inch sieve and sifted through a 40-mesh sieve (15 holes per cm.). The coarse and fines are then weighed and the required number of reserve samples put up with proportionate parts of coarse and fines in separate bags. The samples for assay then consist of two parts, respectively coarser, and finer, than the 40-mesh sieve. In weighing for the gold and silver, the assay is made up with the coarse and fines in proper ratio, but the copper assay is made on each part separately and the correct assay figured.¹

For pure and fairly homogeneous material, the borings are ground as before, but are cut directly without sifting by means of a split sampler or riffle with $\frac{1}{4}$ -inch divisions. Some operators divide to two samples of 40 grams each, others reduce further until a portion is obtained of one "assay ton" (29.167 grams)

¹ Method used by Raritan Works, Ledoux & Co., and Calumet & Hecla.

for the gold-silver assay and 80 grams for duplicate electrolyses, which will include the proper amounts of the finer and coarser parts. Samples "dipped" from a bottle, or from a layer spread out on paper, will not contain the correct proportions of coarse and fine drillings.¹

Solubility of Gold. — It is now generally conceded that the old nitric acid method gives low results for gold. According to F. P. Dewey,² even the purest gold is slightly soluble in nitric acid if boiled for some time. Dr. E. Keller has observed with regard to gold in copper bullion³ that gold is soluble in varying degrees in nitric acid, the solubility diminishing with faster cooling of the copper and reaching a minimum when the molten bullion is quenched in cold water, although a deficit still exists as compared with the fire assay. Accordingly, the fire assay was generally specified for gold before the introduction of the mercury-sulphuric acid method. There is one advantage: the fire assay by scorification is applicable to all grades of copper.

1. Fire Assay for Gold.⁴ — Weigh out 4 portions of borings of .25 "assay ton" each (7.5 grams), mix with 50 grams of test lead, transfer to 3-inch Bartlett scorifiers, cover with 40 grams of test lead, and add about 1 gram of silica. Scorify hot, heating at the finish so as to pour properly. Add test lead to make the weight of button plus lead equal to 70 grams, add 1 gram of silica, and scorify for the fifth time. The button should be free from slag and weigh 14 grams. Cupel at a temperature to feather nicely and raise the heat at the finish. Use a cupel of medium hardness, made of 60-mesh bone-ash.

Weigh the bead and place it in a test tube, add about 10 c.c. of nitric acid (1 acid (d., 1.42) to 5 volumes of water). Place the tube in a beaker of water and warm until action ceases, then bring the water to boiling. Pour off the acid and wash with distilled water three times, then transfer the gold to a porcelain crucible, dry, anneal, and weigh. The two results should check within .02 Troy ounce per ton of 2000 pounds —

¹ Method used by U. S. Metals Refining Co., also Ledoux & Co.

² *J. Am. Chem. Soc.* **32**, 318.

³ *Bull.* **80**, *A. I. M. E.* 2093, and **83**, 2738.

⁴ Smoot & Greenwood, personal communications — same as author's method.

the average figure to be reported. If the silver contents of the bullion are low, add enough fine silver to the copper borings before the first scorification to make the total silver in the mixture equal to about eight times the gold. The objection to any all-fire method is the small size of the sample.

2. Western Assay for Gold in Crude Copper.—In this modification the sample is made very small to avoid scorification, but a number of portions are taken from each package, usually ten portions of .05 assay ton each. Place them directly in cupels. Fill the cupels with test lead. Open the cupellation at a very high heat, having very little coal on the grate bars. Reduce the heat very quickly and cupel at a moderate temperature. Part and weigh the beads in two sets of five, if preferred. The cupels used are 1.5 inches (3.8 cm.) in diameter and 1.12 inch (3.8 cm.) in height.

3. The Mercury-Sulphuric Acid Method.¹—This is a standard assay for gold, silver, and platinum which is, however, applicable only to high converter blown metal, or well-refined copper. It tends to give high silver results, owing to the presence of copper in the silver bead (Greenwood). According to the experience of several laboratories, the acid process with amalgamation is the best universal method.

The modification employed by Greenwood, Smoot, and the author is as follows:—Weigh out three portions of the fine borings of one assay ton (29.167 grams) each, and assay each separately. Place each sample in a 750 c.c. lipped beaker and cover with a watch-glass. Treat the sample with 10 c.c. of mercuric nitrate (or 25 c.c. of the saturated acid sulphate described in 17, Chapter III). Rotate the beaker until the copper is thoroughly amalgamated, then add 90 to 100 c.c. of sulphuric acid (d., 1.84), placing the beaker on a hot plate or burner, and boil until the copper is dissolved to a paste. Converter drillings require about twenty minutes, refined metal one half-hour. Remove the beaker and allow it to cool to a semi-liquid sludge. When cool, add about 500 c.c. of hot water, stir until the copper sulphate dissolves, then add 4 to 6 c.c. of salt solution (1 c.c. equals 50 mg. of silver), or an equivalent amount of hydrochloric acid. Stir well and filter at once (or within fifteen minutes) through a triple 15 cm. filter, or a 7 cm. S. & S. 598 doubled filter. Wash out the beaker with hot water,

¹ S. N. Scott, Jr., *Mines and Minerals*, 1910.

then wipe the inside with filter paper, and add the pieces to the filter. Thorough washing of the filter itself is not necessary.

Transfer the wet filter and contents to a 2.5 inch scorifier in the bottom of which is a piece of sheet lead about 2 inches (5 cm.) square. Some operators omit the lead foil, but instead, give the scorifiers a preliminary glaze with pure melted litharge to prevent the silver from sticking to the bottom. Burn off the paper at a low heat, best in a closed oven heated to nearly 350° C. This chars the paper slowly below the melting point of silver chloride, and therefore without any danger of loss of silver. The author obtains a better reduction by dusting 2 grams of powdered lead on the inside of the paper before incineration. When the paper is entirely consumed, add 30 grams of test lead and scorify, pour at the right time to obtain a 12 to 15 gram lead button, and cupel the lead. The cupel should show good "feathers." It should be made of 60-mesh bone-ash and of medium hardness. The writer prefers the Brownite cupel, which absorbs less silver in the direct cupellation of silver chloride.

Part the gold as in method (1), and subtract the weight of the gold from that of the original bead, the difference being the silver. Greenwood insists that the bead must be inquarted with additional silver if the silver is lower than five times the gold. The two results on gold should check within .02 ounce per ton and the silver within 1 per cent of its own weight. The average of the two results for each metal to be reported. If platinum exists in the copper, separate it from gold by one of the special methods (9 and 10, Chapter VIII).

*Limits of Accuracy.*¹—The mercury salt is added to promote solution and prevent formation of sulphide of copper. None of the silver is carried into solution unless the heating is too long continued after the copper is dissolved, or unless the silver is more than 60 to 70 ounces per ton of copper. In these cases, a small amount of silver is apt to be dissolved, but even in copper containing up to 150 ounces per ton, the silver results on such metal will be fairly comparable with those of the nitric acid method, although, on the whole, averaging a little lower.

If the silver is much in excess of 50 ounces per ton, even the addition of salt solution will not precipitate absolutely all of the silver. The gold results agree closely with those of the quarter

¹ Communicated by A. M. Smoot.

assay ton all-fire method on most coppers (which can be sampled correctly with as low a quantity as .25 assay ton). Some very impure material — especially if it contains much arsenic, antimony, selenium, and tellurium — may yield results a little lower than by the dry method.

With such impure copper, better results will be obtained by melting the silver precipitate in a 10-gram crucible with a flux used in western reduction works and recommended first by Scott. Burn the papers at a low heat and flux with 15 grams sodium carbonate, 7.5 grams potassium carbonate, 1.5 grams borax glass, 1.5 grams silica, 1.5 grams flour, 30 grams litharge. Place the crucible in a muffle or pot at a low heat and finish at a high heat, — time, twenty to twenty-five minutes.

4. Method with Potassium Bisulphate and Sulphuric Acid. —

This assay is based on another scheme for the solution of the copper without loss of gold. It has the single advantage in certain cases, that the solution may be subsequently employed for the estimation of arsenic and nickel, or zinc. Place one assay ton of *very fine* borings in a 750 c.c. lipped beaker, add 30 grams of potassium bisulphate crystals and 100 c.c. of sulphuric acid (d., 1.84). Boil for half an hour, so rapidly that the foam half fills the beaker. When the foam lessens and the metal appears to be dissolved, grasp the beaker with a holder made from a piece of harness strap (1 inch by 12 inches), and whirl it until any black sulphide is washed down from the sides. Boil for ten minutes to destroy the black sulphide, then proceed as in the mercury method, melting the residue with the crucible flux.

If a trace of copper still remains undissolved, transfer it to a No. 3a casserole and boil it with 3 grams of bisulphate and 10 c.c. of acid. There is a tendency for insoluble sulphide to remain also, and the boiling must be carefully watched. Owing to the small amount of sulphide precipitated with the silver, the reduction of silver in very rich material should be more complete than in the previous method.

5. Nitric Acid Method for Silver in Metallic Copper. —

As nitric acid has a slight solvent action on gold, this assay is only depended upon for the silver contents.¹

¹ Modification of A. M. Smoot and F. D. Greenwood.

Weigh out two portions of copper borings of one assay ton each and place them in 750 c.c. lipped beakers. Add 100 c.c. of water and 90 to 100 c.c. of nitric acid (d., 1.42). The acid may be added in small portions of 30 c.c. each at intervals of about one hour, if the gold is to be determined this way. Otherwise, add the acid in portions of 50 c.c. If gold is present, precipitate a small amount of silver chloride with standard salt solution in order to collect the gold, then filter through double filter papers when settled, and wash the papers free from copper. (One may filter the solution from gold without the collector of silver chloride.) The beaker is finally wiped with paper, adding this to the filter. Transfer the gold precipitate to a Bartlett shape scorifier, which contains a lining of sheet lead, or has been glazed on the inside with molten litharge. To the filtrate, add a calculated amount of sodium chloride solution as in former methods, but avoiding much excess. Stir well, and allow to stand several hours, better, over night. If the silver present is less than 50 mg. (50 ounces per ton), the silver chloride is apt to remain too finely divided.

Some operators add 5 c.c. of sulphuric acid followed by 3 c.c. of a saturated solution of lead acetate and stir briskly for several minutes, allowing to settle as usual before filtering. It is, however, better to avoid the use of a collector if possible. When the silver only is required, the precipitating reagent may be added to 400 c.c. of water in a separate beaker, and poured quickly into the hot syrupy nitrate of copper, avoiding the sides of the beaker. The solution is then heated rapidly on the hot plate and boiled one minute, with the result that the silver is clotted sufficiently to filter clear after settling. When the supernatant liquid is quite clear, filter through double filters, or a 598 S. & S. 7 cm. filter supported on a platinum cone with coarse perforations. Wash the beaker, wipe it with filter paper or a large camel's hair pencil, and heat the last washings to boiling before filtration. Wash the papers free from copper salt, transfer all filters to the scorifier containing the gold.

Five grams of powdered test lead may be sprinkled inside the silver filter (Greenwood). Dry and ignite the papers very carefully at a low heat, best in a closed oven heated to a temperature which will cause the paper to char without flaming, or

about 300° C. As silver chloride melts at a temperature one hundred degrees higher than lead, there will be no loss of silver below the point at which the lead melts down.

On removing the scorifier to the open air, the carbon will glow gently until consumed. Add 25 to 35 grams of test lead to the ash with .5 gram of borax, and scorify at a low heat just long enough so that the resultant button shall weigh 12 to 15 grams. The button should then be cupeled at a low heat so that the feather litharge completely surrounds the bead. The cupel should be made of bone-ash ground to pass a 60-mesh sieve and should be of medium hardness.

Part the weighed beads of gold and silver as in the previous methods. Pour off the first (1 : 5) acid, wash once with distilled water, and then place the tube in a beaker of water and boil for half an hour with nitric acid (d., 1.30) (Smoot), or possibly with acid (d., 1.42) as recommended by Greenwood. Pour off the strong acid and wash three times with distilled water. Place the gold in a porcelain crucible, dry, anneal, and weigh as usual, taking the silver by difference. If the gold is more than one-fifth of the silver, the bead must be inquarted. The two results on gold should check within .02 ounce per ton and the silver within .5 per cent of the amount present, taking the average of two results in each case.

6. Rapid Assay; Direct Cupellation of Silver Chloride.¹—

The product of most of the Lake Superior refineries is tested by direct cupellation. The loss due to scorification is nearly eliminated. Higher results with this process are obtained by using Brownite cupels, in which the lime and magnesia have a reducing effect on silver chloride not possessed by bone-ash.

Dissolve about 29 grams, or 1 A. T., of drillings in a 750 c.c. beaker with 150 c.c. of nitric acid (d., 1.42), added in three portions of 50 c.c. The beaker is placed on the hot plate, the red fumes boiled out, and the beaker immediately removed. The requisite amount of salt, or hydrochloric acid to provide a slight excess, is placed on the bottom of a 500 c.c. beaker and covered by 400 c.c. of water. The water is now poured quickly into the hot copper solution, without touching the sides of the container. Boil for one minute, cool, and settle over night. Filter on a 598 S. & S. 7 cm. paper, supported by a coarsely

¹ *Trans. A. I. M. E.* **31**, 484.

perforated platinum cone. Wash, filter, etc., as in the preceding method.

Cupellation.—Dust the inside of the moist filter with 1.5 grams of 30-mesh lead. Store the filters in a funnel rack until the muffle is ready, then fold each one before charring, and place it, point down, in a 1.25 inch (3.2 cm.) Brownite cupel. These give higher results than bone-ash as already explained. The charring should be done in a separate muffle at very low red heat. The empty cupels should be placed in the hottest muffle for half an hour before use, and then brought down to the temperature of the cooler muffle before charring the filters. A very little lead is placed under the paper, also.

When a gray ash remains, add 4.5 to 5 grams of lead, transfer to the hottest muffle, melt down quickly, bring forward and finish in a single row at a low heat. At the same time, another set is being charred in the cooler muffle.

The beads must be pushed back into the hottest part of the muffle about 15 seconds before the “blick,” to remove the last trace of lead when using this make of cupel. One operator uses potassium bromide as a precipitant, but the actual loss of silver due to the solubility of the chloride, alone, is only .1 to .12 Troy ounce per ton of copper.

If a corrected assay is required, silver chloride from weighed foil may be cupeled as proofs, or the average cupel correction may be determined for a month's run of assays of uniform material, by crushing and assaying all the Brownite cupels used during that time.

THE ELECTROLYTIC ASSAY OF CRUDE COPPER

In the assay of refined metal (Chapter XI), 5 grams of drill-
ing are directly dissolved in a standard acid mixture, and the whole electrolyzed. In order, however, to obtain an average sample of crude metal such as slabs or anodes, it is necessary to derive the final assay weight by riffling down a large sample to 80 grams, or to two portions of 40 grams each. These portions are weighed, dissolved, and an aliquot portion of the diluted solution electrolyzed.

Aliquoting Apparatus, — Automatic Pipettes.—In Chapter I, the most suitable types of stands, flasks, and pipettes are described. The manner of mounting the Smoot “wash-out”

pipette is illustrated by its designer in Fig. 13. The water-jacketed type is fully described in a paper by W. C. Ferguson.¹ Each has its advocates, but the writer prefers the former, which is not so elaborate. In mounting, it is best to have the filter pump connected with a large vacuum reservoir fitted with a mercury trap which maintains a vacuum equivalent to about 3 inches, or 75 mm., of mercury. This pressure is sufficient to work the apparatus rapidly.

The vacuum reservoir should be connected to a large bottle for holding waste liquid, which is drawn over in filling and washing the pipette;—this is shown in the cut, directly behind the support. The sides of the delivery tube are parallel instead of tapering to a small orifice. This facilitates rapid filling and delivery and also gives a sharp cut-off at the end when the pipette is full; that is, the solution is exactly parallel with the bottom of the glass tube, and there are no air bubbles which sometimes occur when the lower end is constricted. Repeated measurements are practically identical, provided that the temperature of the liquid does not vary.

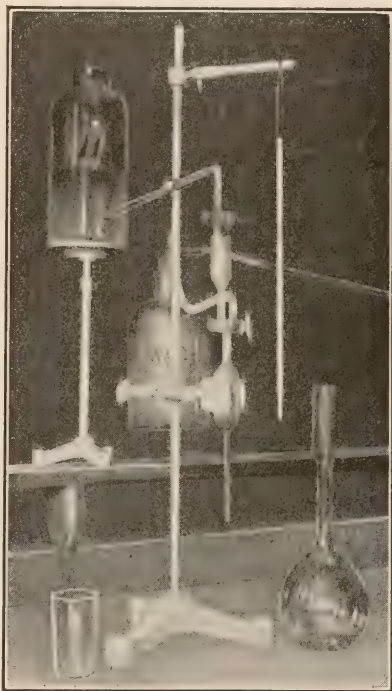


Fig. 13.—Smoot Automatic Pipette.

Standardizing.—For aliquoting solutions of copper, liter flasks and 50 c.c. pipettes are the most convenient volumes, the unit size being the Mohr liter, true liter, or any similar volume. The important point is that the pipette shall hold an exact fraction of the contents of the flask;—in this case, one-twentieth. It is impossible to obtain apparatus sufficiently accurate from the makers, and the chemist should standardize his own. Pipettes may be ordered to hold rather more (say about .1 c.c.) than one-

¹ *J. Ind. and Eng. Chem.* **2** (1910), 187.

twentieth of the volume of the flasks. The number of liter flasks required will depend on the amount of work to be done per day, but two pipettes will be sufficient for any number of flasks, the second pipette being held in reserve.

Clean and dry all the flasks and select any one of them as a standard. Counterpoise it on a balance which has capacity of 2000 grams and a sensibility of at least .02 gram. Fill the standard flask with water at room temperature exactly to the mark, and then counterpoise the added water by pouring test lead into a bottle placed on the other pan. The bottle of test lead then represents the weight of the water. Remove everything from the balance and counterpoise another empty flask; replace the bottle of test lead and add water at room temperature to the empty flask until it balances with the bottle of lead. Make any necessary changes in the mark to bring the capacity of the second flask to that of the first. By proceeding in this way with all the flasks, they may be made to have exactly the same capacity as the first standard flask, and this is accomplished without any errors that might be due to inequalities in the balance beam, or errors due to temperature, provided that the water remains at a uniform temperature. Any trace of water on the inside of necks must be removed before the final balancing.

The graduation of the pipette to the flask is best done by working on pure copper. To this end, a standard copper of known copper and silver content should be taken. Selected wire bar turnings with a content of 99.95 per cent make the best standard. The exact content should be ascertained by making a number of assays by the "five gram" method of Chapter XI. Then weigh 40 grams of the standard copper into the standard liter flask and dissolve it in a mixture of 200 c.c. of water, 120 c.c. of nitric acid (d., 1.42), and 20 c.c. of sulphuric acid (d., 1.84), adding the nitric in two portions of 60 c.c. Boil the liquid, cool to room temperature, and dilute to about 950 c.c. Mix the liquid by rotating the flask, and test with a thermometer graduated in fifths of a degree C., to be sure that the temperature is normal. Dilute to the mark and mix thoroughly by stopping the neck of the flask with a well-fitting rubber stopper, inverting and shaking several times, and testing the temperature again after mixing. Have the pipette mounted in a place free from

draughts where the thermometer does not vary more than 1°C . As there is always a difference between the upper and lower parts of a room, the flasks should be kept near the level of the pipette, which is connected to the filter pump as illustrated.

Pour about 300 c.c. of the copper solution into a No. 3 beaker and fill the pipette by placing the stem in the beaker and turning the stop cock so that the right-hand bore connects with the waste bottle and the filter pump with the bulb, and fill the pipette, letting a little liquid run over into the waste bottle. Remove the beaker and turn the stop cock so that the funnel opening connects with the bulb, running the liquid to waste. Repeat this operation, thus washing the pipette twice with copper solution. Fill the pipette a third time in the same way and make sure that no air bubbles appear in the stem immediately below the stop cock. Remove any solution adhering to the outside of the stem with a piece of soft paper, being careful not to touch the opening in the stem with the paper. Run the solution into an electrolytic beaker, and wash the pipette with three successive portions of water of 10 c.c. each introduced through the funnel, letting the wash water run into the main liquid. Make three or four aliquots in this way and determine the copper in each electrolytically, just as with the standard copper, making the necessary additions of water and acid to secure the best conditions.

If the pipette was made a little too large, as it should have been, the copper obtained will weigh more than one-twentieth of the amount weighed into the standard flask, but three or four assays made in this way should not vary more than .0003 gram between the maximum and minimum weight. Determine the capacity of the pipette per running centimeter. This may be done either by using standard copper solution and making several estimations of copper, contained in the liquid measured from a small mark scratched on the stem near the bulb to the end of the stem; or it may be done by weighing some water into a small flask, filling the stem from this flask to a mark and weighing the flask again, taking the weight of the water by difference, and calculating the volume. Calculate the number of cubic centimeters that must be cut from the lower end of the stem to reduce the holding capacity of the pipette to the required volume, and by means of a sharp file cut off about two

millimeters less than the required length. Grind the edges of the tip square by rubbing the end against emery cloth stretched on a plane surface and redetermine the capacity of the pipette in relation to the standard flask by standard copper, as before. The pipette should now hold very slightly more than one-twentieth of the volume of the flask. A little judgment will show how much more should be taken from the stem to bring the capacity exactly right, and this small amount should be removed by grinding with emery.

Finally, the accuracy of the pipette should be tested by aliquoting from several 40-gram portions of standard copper dissolved in the same flask as before. All the tests should agree within .02 per cent. The question of temperature is very important in this work and all the operations, in which it could affect the results, should be checked with a thermometer. The pipette may be water-jacketed if desired (like the instrument devised by Ferguson), but this precaution is hardly necessary since a variation of 1° C., or even more, in the room temperature does not perceptibly affect that of the solutions within the time required for mixing and aliquoting. Several of the other flasks should be checked against the pipette in the same way and one or two of them set aside as standards, so that future purchases of flasks may be standardized easily to the pipette. The second pipette should be standardized like the first and held in reserve in case of breakage.

At any time, the capacity of any flask may be checked against the pipette by means of the standard copper, and it is well to run at least one standard a week to make sure that no change occurs in the relative capacities. The pipette should be cleaned daily by filling it with strong sulphuric acid saturated with potassium bichromate, and a very little vaseline may be used as a lubricant for the stopcock.

THE ASSAY OF CRUDE COPPER BY ELECTROLYSIS

7. Converter Slabs and Blister. — A. M. Smoot and F. D. Greenwood describe the same methods and use the same pipettes, and the procedure of the majority of refineries is based on a scheme similar to the one to be described. This modification is intended for 99 per cent metal which does not contain a proportion of impurities which would be sufficient to interfere

with the direct electrolysis of the original solution of the sample. The sample should be ground to pass at least a $\frac{1}{16}$ -inch sieve (Chapter II), and that part of the borings which is finer than 60-mesh should contain at least 95 per cent of copper; that is, the sample should be quite homogeneous. For heterogeneous, or variable metal, method 8 should be used.

Divide the sample repeatedly on a split sampler having quarter-inch (63 mm.) divisions until two portions of about 40 grams each are obtained by a coarse balance. The division should be made within about .5 gram of the required weight so that only a small amount need be added to, or taken from, the sample to bring the weight to exactly 40 grams. In this division, loss of dust must be avoided and great care must be used to mix the sample after each division so that coarse and fine parts will be cut out in equal proportion.

Adjust the weight on an analytical balance to exactly 40 grams by a spatula and transfer to a liter flask. Add 200 c.c. of water, 60 c.c. of nitric acid (d., 1.42), 20 c.c. of sulphuric acid (d., 1.84); when the action has subsided add 60 c.c. more of nitric acid, and sufficient sodium chloride solution to precipitate all the silver present. Thus, in copper containing about 80 ounces of silver per ton, an amount of sodium chloride equivalent to 100 ounces of silver may be safely added or 6.5 c.c. of N/5 sodium chloride.

Set the flask in a warm place until the copper is dissolved, then boil the liquid until the red fumes are expelled, cool to room temperature, dilute to about 925 c.c., mix the liquid well by rotation without spattering, again test the temperature, and finally adjust the volume exactly to the mark. Now close the flask with a rubber stopper and mix by inverting and shaking several times. Filter a portion of the liquid rapidly through an 18 cm. folded filter (S. & S. 588) into a clean dry beaker. Reject the first 100 c.c. of filtrate and from the next 300 to 400 c.c. take 50 c.c. (or 2 grams of sample) by means of the pipette described above. Add to this portion, 2 c.c. of a mixture of equal parts of nitric acid (1.42) and sulphuric acid (1.84), dilute to 130 c.c., and deposit the copper on perforated platinum cylinders, using .35 ampere for about eighteen hours.

The electrolytic beaker should be covered during the time of deposition with a closely fitting split watch glass, which is

washed down with a fine stream of water after sixteen hours. If the assay is nearly finished, the newly immersed surface of the cathode will remain quite bright, but if more copper is present than can be deposited in two hours, the stem will be discolored in about half an hour. This serves well enough as a practical guide, but the electrolyte should finally be tested with hydrogen sulphide after the electrodes have been withdrawn. Disconnect the cathode very rapidly, substituting a beaker of water, or plunging the cathode under water, rinse several times, drain over blotting paper, rinse it with alcohol, drain again, and dry over a Bunsen flame, being careful not to use sufficient heat to oxidize the deposit. Cool and weigh the copper.

In testing the electrolyte with hydrogen sulphide, an experienced eye can usually detect .0002 gram of copper, even in the presence of some arsenic and antimony. Any weighable deposit should be filtered off, calcined, dissolved in nitric acid, and the copper estimated by the color test if desired, though this extra work is rarely necessary. Duplicates made in separate flasks from the beginning, should check within .05 per cent; duplicates taken from the same flask, within .01 per cent or .02 per cent.

This method does not include insoluble copper which is rarely found in converter bars. (Each brand of copper should be tested as some nickeliferous copper leaves a residue from nitric acid solution consisting of oxides of nickel and iron.) In such a case, the sample should be dissolved in a large beaker, the liquid filtered into the liter flask, and the ignited residue fused with a little potassium bisulphate in a porcelain crucible, adding the water solution of the melt to the flask.

It will be observed that no account is taken of the volume of the insoluble residue, or of the silver chloride in the liter flask. Usually, these are too small to be considered, since bar copper rarely contains more than .10 per cent of insoluble matter, nor would silver chloride equivalent to 100 ounces per ton appreciably affect the liquid volume.

F. D. Greenwood makes no allowance for the volume of the silver salt unless the silver runs over 600 ounces per ton. The possible evaporation of the liquid during filtration is a source of error, but many experiments by Smoot and Greenwood have shown that it is negligible if the filter is kept full and the work is done rapidly.

8. Non-homogeneous Metal. — When wide differences exist between the coarse and fine parts of the ground sample, as when much cuprous oxide from overblown copper is present or when the metal contains considerable nickel, the method of direct splitting should not be employed (see preparation of samples). In such cases, the whole ground sample should be weighed and sifted through a 40-mesh screen (see copper sampling, Chapter II). The final samples should consist of accurately weighed portions of the "coarse" and "fines," and the 40-gram charges should be made by weighing proportionate parts of each; otherwise the procedure is the same as in modification 7.

9. Low-grade Bars, By-products, Leady Mattes, etc. — In these products, the bars contain excessive impurity which interferes with direct electrolysis. According to Smoot and Greenwood, either of the foregoing modifications may be employed for obtaining the weighed sample, depending on the character of the borings.

Method. — Dissolve forty grams of the sample, contained in a large beaker or flask, in a mixture of 200 c.c. of water and 120 c.c. of the strong nitric acid, adding the latter in two portions of 60 c.c. each. Greenwood also adds 20 c.c. of sulphuric acid. Precipitate the silver as usual, and boil vigorously, filter into a flask, and wash the residue well with hot water so that all soluble copper is obtained in the flask. Remove the flask and wash the residue with hot sodium thiosulphate to dissolve silver chloride.

Wash the residue again with water, dry, ignite, and fuse it in a porcelain crucible with potassium bisulphate at least one-half an hour to dissolve nickel. Dissolve the fusion in water, add a very little sodium chloride to remove any silver that may have escaped solution in the sodium thiosulphate, then boil and filter into the main solution. Cool to room temperature, make up to volume, and take out 50 c.c. for test.

A. M. Smoot adds at this point a pure solution of ferric nitrate containing sufficient iron to retain all arsenic, antimony, selenium, or tellurium, .2 gram usually being required. Make the liquid alkaline with excess of ammonia, stir well, and allow the mass to settle on a steam bath for half an hour. Filter and wash the residue with dilute ammonia. The greater part of the

copper is in the solution; set it aside, or, if the volume is too large, reduce it by rapid evaporation.

Dissolve the ferric hydroxide in hot dilute hydrochloric acid, nearly neutralize with ammonia, leaving it, however, slightly acid, add 40 c.c. of a saturated water solution of sulphur dioxide, and set the liquid in a warm place for half an hour until the iron is reduced to a ferrous condition. Then add 2 c.c. of a 15 per cent solution of potassium thiocyanate (150 grams per liter).

Allow the cuprous salt to settle for half an hour in a warm place, filter through a doubled 9 cm. paper, and wash the salt once with warm water, containing 2 per cent of ammonium nitrate. Transfer the filter to a No. 2 porcelain crucible, dry slowly, and ignite gently in a muffle, beginning at a very low temperature. After the paper is burned, raise the heat gradually until the carbon is all consumed, then cool, add 3 c.c. of water and 6 c.c. of nitric acid. Set the crucible on a steam bath until the copper oxide is all dissolved and the solution is clear. Boil for a few minutes, and add the liquid to the main solution.

Acidify the liquid, if necessary, by adding (1:1) sulphuric acid until it is faintly acid, then add 6 c.c. of strong nitric, adjust the volume to 130 to 180 c.c., and electrolyze as in modification 7.

NOTE. — Nickeliferous residues may be dissolved by boiling with 10 c.c. of sulphuric acid, 5 c.c. of nitric, and 3 grams of potassium bisulphate. Dilute, heat to boiling, filter, and add filtrate to main solution. It is better to omit the ferric nitrate if possible from assays of nickeliferous copper. Add more acids before electrolysis.

10. Assay of Crude Copper Containing Selenium or Tellurium. — If much tellurium is present it would contaminate the copper, and the method may be modified as follows:

Proceed with the blister, or converter, drillings as in method 9 until the hydrochloric acid solution of the ferric hydroxide has been obtained. To the iron solution add about one gram of tartaric acid in solution, then add sodium hydroxide until the liquid is faintly alkaline. Pass a rapid current of hydrogen sulphide which will precipitate copper and iron as sulphides but retain arsenic, antimony, selenium, and tellurium in solution. Filter on a 12 cm. paper and wash once or twice with a 2 per

cent solution of sodium sulphide free from polysulphides. Transfer the mass back into the beaker by means of a fine jet from a wash bottle, and add 10 c.c. of hydrochloric acid (d., 1.20), which will dissolve the ferrous sulphide but leave the copper. Dilute the solution with 100 c.c. of hydrogen sulphide water to make sure that all the copper is precipitated, stir well, and filter through the same 12 cm. paper that held the sulphides originally. Wash the copper sulphide with water, transfer the paper and contents to a large porcelain crucible, dry, and ignite at a low temperature until the carbon is burned off. Dissolve the mixed copper oxide and sulphide in dilute nitric acid and proceed as in 9.

NOTE. — In the absence of much bismuth, one may employ the more rapid method of the author, described in the assay of refined copper (Chapter XI). This is simply a direct precipitation of the selenium and tellurium from a sulphuric acid solution of the sample with sulphur dioxide, omitting the precipitation with ferric hydroxide, but using sufficient acids in the final electrolyte to hold up the arsenic and antimony present.

11. Separation of Copper as Thiocyanate. — This method is included as an alternative. The separation of impurities, except tellurium, is quite complete, but the operation is tedious.

Proceed as in modification 9 until the final 50 c.c. portion is obtained in a 500 c.c. beaker. Make this strongly alkaline with ammonia, adding the reagent until the copper hydroxide redissolves, then make acid with hydrochloric, adding about 2 c.c. in excess. Now add 50 c.c. of saturated sulphur dioxide solution, dilute to 300 c.c., and then add at once 20 c.c. of potassium thiocyanate (15 per cent solution), stir well, and let the mixture stand on a bath at 80° C. for an hour and a half, or until the mass settles, leaving a clear liquid above. Filter on doubled filters, using a 15 cm. paper inside and a 12.5 cm. paper outside, wash with a warm 2 per cent solution of ammonium nitrate, transfer the filter and contents to a large porcelain or fused silica crucible, dry slowly in a muffle, and ignite as in previous methods. Dissolve in nitric acid.

F. D. Greenwood modifies the method of Smoot by taking one-twentieth of a 20-gram sample to avoid the treatment of a large bulk.

Dissolve a 20-gram sample in 10 c.c. water, 60 c.c. of nitric

acid, and 10 c.c. of sulphuric acid, add sodium chloride to remove all silver, and boil to expel red fumes. Then dilute to mark and draw out one-twentieth, equal to 1 gram of copper. Evaporate to fumes, dilute to 200 c.c., neutralize with ammonia, make slightly acid with sulphuric acid (or hydrochloric in presence of arsenic). Pass sulphur dioxide gas through the boiling solution until all the iron and copper have been reduced.

In four or five minutes, the copper may be thrown down as thiocyanate, but pass the gas until the mass is perfectly white. Boil and settle until clear, then filter and wash. Dissolve with nitric acid, evaporate to fumes with 10 c.c. of sulphuric acid, dilute, transfer to a tall beaker, add 4 c.c. of ammonia and 5 c.c. of nitric acid, and electrolyze over night.

12. Purification of Cathode by Second Electrolysis.— This simple means of purification may be used to obtain a final pure weighable copper deposit in cases where the interfering impurities are arsenic and antimony, only. The first cathode deposit is placed, without weighing, in another electrolytic beaker, covered with water and 40 c.c. of acid mixture (see Chapter XI), and the electrolysis repeated as soon as the copper is dissolved. The beaker is carefully covered with a watch glass perforated with a small hole just large enough to pass the stem of the electrode.

FOREIGN METALS IN CRUDE COPPER

Nickel must be estimated frequently in crude material. This element may be recovered from the electrolyte remaining from the electrolysis of copper. The wash waters and test portions should be saved and the combined solutions evaporated to fumes with 10 c.c. of sulphuric acid. The diluted solution is then made strongly ammoniacal and electrolyzed as directed in Chapter VII, method 2.

Cobalt and zinc deposit with the nickel. They may be separated from the nickel, either before, or after, electrolysis by methods 4 and 5, Chapter VII.

To avoid repetition, the determination of all other impurities in crude metal will be included with the analysis of refined copper in Chapters XII and XIII. The only essential difference in tests of crude metal is the reduction of sample weights from 50 or 100 to a limit of 2 to 20 grams, and the occasional necessity for examination of insoluble residues.

PART III

CHAPTER XI

THE ELECTROLYTIC ASSAY OF REFINED COPPER

THE DETERMINATION OF COPPER

The Electrolytic Assay of High-grade Copper.—The first requirement of an exact technical method is that the sample shall be small enough to permit direct electrolysis without division by pipettes, but large enough, however, to neutralize the errors of manipulation and thus permit duplicate tests to check within the limit of .015 per cent. Recently, the Alloys Committee of the American Chemical Society has recommended the 5-gram assay as a standard with this limitation of accuracy.

The second requirement is that an assay started at the close of business must finish about noon of the next day. The acids and water should be strictly free from chlorides. It is much safer to complete the washing of electrolytic beakers by rinsing them with distilled water, and placing them on wooden pegs to drain, than to attempt to dry them with cloths.

When refined copper is treated with dilute acids, some impurities may remain insoluble (as noted in 9, Chapter X, and in the first page of the next chapter), but not usually in sufficient amount to enclose any copper.

Elements Determined.—In tests of refined metal, it is customary to deposit and report the silver with the copper. This works well up to a limit of .3 per cent of silver, or 100 ounces per ton.¹ The methods in general use in the United States are, *First*, the exact 10-gram assay; *Second*, the standard 5-gram assay for routine work; *Third*, the rapid assay with some rotary device.

1. The Ten-gram Assay.—According to this modification, devised by F. Andrews, ten grams of drillings of cast copper are weighed into a tall lipless beaker of 500 c.c. capacity and

¹ Keller; Heath.

dissolved in 50 c.c. of water and 35 c.c. of nitric acid (d., 1.42). When solution is complete, the glasses and beaker are carefully washed down and the solution evaporated until all the free acid is driven off and the crystallizing point reached. After cooling, add 100 c.c. of water, 10 c.c. of ammonia (d., .91), then 6 c.c. of sulphuric acid (d., 1.84), and make the solution up to 275 to 300 c.c. Make the deposition on a platinum cylinder which

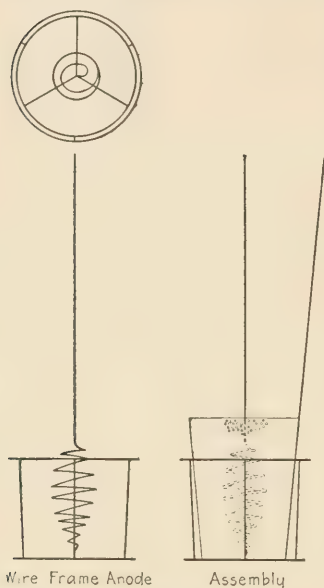


Fig. 14.—Special Electrodes.

may be 2.25 inches (5.7 cm.) in height and 1.6 inches (4.1 cm.) in diameter, of about 15 grams weight, and perforated with 24 holes to the linear inch (1 per mm.)—Fig. 14. Keller¹ recommends about seven .5 mm. holes to the inch (25 mm.). Use a current of 1 ampere per assay from the lighting circuit. In the morning, after fifteen hours, wash down the split watch glasses and sides of the beaker, and watch the clean cathode stem, thus exposed to the liquid, for one-half hour. If no copper is deposited, withdraw 1 c.c. of solution and test it on a spot plate with hydrogen sulphide water. The copper is generally deposited in sixteen hours, only the slightest gassing is ever observed at the cathode, and no

impurity has ever been found by Andrews in the deposited copper.

The experience of the author shows that it is easier to dissolve the copper in 70 c.c. of the acid mixture given in the "five-gram method" and, since a trace of copper is always retained in the electrolyte, it is more accurate to cut the volume of electrolyte down to about 175 c.c.

Other precautions in manipulation are described in the next methods.

2. The Standard Five-gram Electrolytic Assay.—This description follows closely a report of the Alloys Committee of the

¹ *Bull.* 80, A. I. M. E., 1913, 2093.

American Chemical Society on a standard method for the battery assay of copper. The author¹ proposed a standard acid mixture for dissolving copper, which should permit direct electrolysis without evaporation, and should provide a sufficient excess of sulphuric acid to hold back the impurities until the assay is finished, notwithstanding the reduction of much of the nitric acid to ammonia by the electric current.

General Instructions.—Six ingots, or other castings, are selected at random from a lot and drilled through, without oxides, as directed in Chapter II. Weights should be calibrated and frequently re-checked. It is recommended² to use a special 5-gram brass weight in weighing the samples and to have the weight of sample always within 5 mg. of 5 grams. When the cathode with its deposit is finally weighed, the identical weights are to be used with which the cylinder was tared, plus the special 5-gram brass weight. This brings all the change or deficiency in the final weight on a small fractional weight and the beam and rider.

Electrodes.—The cathode is a platinum sheet of 5 by 10 cm. giving a depositing surface, counting both sides, of 100 sq. cm. This sheet is formed into a cylinder of the open type, and the stem is riveted and soldered with gold to the middle of the sheet. There should be no seam which cannot be cleaned completely by two washings. The anode is made from 1-mm. platinum wire, formed into a spiral of seven turns having a diameter of 12.5 mm. and a height of 38 mm., the stem being straight and 125 mm. long.

Electrolytic and Low-Resistance Lake Copper.—This modification is adapted to the grades of copper covered by the specifications of the American Society for Testing Materials as given in its Year Book for 1913, pages 241–247. The silver is deposited with the copper as in 1, and is included as such; when it is desired to correct for the silver this is determined in a larger separate sample and the amount found is deducted from the total cathode deposit. The deposition of the copper with the silver is said to work well up to the limit of .3 per cent silver or 100 ounces per ton. All assays are to be made in duplicate within an outside limit of .015 per cent.

¹ *J. Ind. and Eng. Chem.* **3**, 74. *Trans. A. I. M. E.* **27**, 390.

² Greenwood, personal communication.

Electrolysis. — Place 5 grams of the clean bright drillings in a tall lipless beaker which is provided with a well-fitting cover glass and add a mixture of 7 c.c. of nitric acid (d., 1.42), 10 c.c. of sulphuric acid (d., 1.84), and 25 c.c. of water. This mixture is used as a stock "Assay Solution," 42 c.c. being measured for each 5-gram sample. The electrolysis beakers are from 100 to 125 mm. tall and 55 mm. in diameter across the bottom, with a total capacity of 225 to 300 c.c. After the assays have stood for a few minutes, and the action has nearly ceased, place them on a steam bath having a temperature of 90° to 100° C. and allow them to remain there until solution is completed and the red fumes have disappeared. Wash the cover and the sides of the beaker, dilute the solution to 130 to 150 c.c. and electrolyze.

NOTE. — (Use of the dilute solution above described prevents a violent reaction and a consequent loss of copper in spray or vapors. This solution should not be boiled, since this likewise may cause a loss of copper.)

During electrolysis the beakers are covered with two pairs of split watch glasses placed at right angles with each other. The current in each solution should be .95 to one ampere, that is 1 ampere per square decimeter, which will require 6 to 10 volts if the assays are arranged in parallel. (The current may also be taken from a 110-volt circuit through incandescent lamps or rheostats as regulators.) It is convenient to start the assays at night; after about fifteen hours wash the cover glasses, electrodes, and beakers and reduce the current to .5 or .6 ampere per solution. As soon as the cathodes begin to evolve gas, reduce the current to .4 ampere per solution. At this time (or as soon as the assay is thought to be finished), take out about 1 c.c. of liquid, place it in a depression in a porcelain test plate, and add 2 or 3 drops of fresh hydrogen sulphide water. If the slightest discoloration occurs, continue the electrolysis, repeating the test until there is no discoloration whatever. If possible the assay should finish without decided evolution of gas.

Without interrupting the current, siphon off the acid solution, at the same time filling the beakers with distilled water. Remove the cathodes quickly, rinse them in distilled water and two successive baths of alcohol. (Redistilled "pyro," or denatured, alcohol gives satisfactory results at much less expense than pure

ethyl alcohol.) An experienced operator can quickly remove a cathode (with one motion) and immerse it in water without loss. Throw off the excess alcohol by a quick motion of the hand and ignite the remainder by bringing the cathode quickly to the flame of an alcohol lamp (or gasoline burner); then keep the cathode moving continually as the alcohol burns. This method of burning off dries the cathode without causing oxidation, whereas drying in an oven at 100° C. generally causes an increase in weight.

NOTE 1. — It has been shown¹ that a few thousandths of a per cent of copper may remain in solution without being detected by the hydrogen sulphide test on the spot plate. This amount of copper is negligible in many instances, but when necessary to make exact determinations, as in the complete analysis of copper, make the solution from the electrolysis slightly alkaline, neutralize with hydrochloric acid (d., 1.19), adding 3 c.c. excess, evaporate to 50 c.c., and precipitate with hydrogen sulphide. Filter off the copper sulphide, treat with nitric and sulphuric acids, and deposit the small amount of copper from this solution by electrolysis and add it to that obtained in the original determination.

NOTE 2. — By the use of rotating anodes, gauze or perforated electrodes, or the Frary solenoid, it is possible to use a high current density and to reduce the time required for depositing the copper to four, or even two and a half, hours. Good results can be obtained by experienced workers, but there is much more chance for error. The slow or overnight method, which is more certain and which requires less of the operator's time, is, therefore, recommended. (A trace of platinum is carried over to the cathode in warm solutions. It may be removed by redissolving the weighed deposit in dilute "solution." Current in solenoid = 4 to 4.5 amperes.) Perfect assays may be obtained by keeping each beaker cold. (See Fig. 10b, Chapter I.)

2b. Modification for Low-grade or Casting Copper. — For all grades of copper which are not included in the specifications of the American Society for Testing Materials, as electrolytic and low-resistance Lake copper, the procedures given below are recommended. These brands may contain a considerable amount of arsenic and some antimony, tellurium, bismuth, and nickel. All

¹ Heath, *J. Ind. and Eng. Chem.* **4**, 404 (1912).

assays are made in duplicate and must check within an outside limit of .015 per cent.

With solutions of such coppers the use of about 2 c.c. of an addition agent prepared by boiling "hard oil" with strong nitric acid, cooling, and removing the grease has been recommended.¹ This, it is said, will permit the use of high-current densities and yet allow the copper to be deposited pure and bright. Moreover, it is said that arsenic and antimony, when present, do not contaminate the copper. It seems probable,² however, that copper deposited from such solutions is not quite pure and that it is more accurate to purify the cathode deposit (modification I below) or to give a preliminary treatment to the solution (modification II).

The committee gives preference to II, and I should be used only in the presence of small amounts of impurities.

Modification I.—Carry out the assay exactly as given for electrolytic and low-resistance Lake copper. Place the cathode in a clean beaker, cover with a watch glass perforated with a small hole, just large enough to accommodate the stem of the electrode, add 42 c.c. of stock "assay solution" and water enough to cover the sheet. Let it stand upon the steam bath until the coating is dissolved. Re-electrolyze in the regular manner.

*Modification II.*³—Dissolve the 5-gram sample in 42 c.c. of the "assay solution" and evaporate until all the nitric acid is expelled. Redissolve in 70 c.c. of water and add 3 c.c. ferric nitrate solution (1 c.c. = .01 gram iron). Transfer the solution to a lipped beaker and place the original beaker under a funnel fitted with a small filter paper. Precipitate the iron from the hot liquid by ammonia, filter, and wash out salts. Place the solution on a hot plate to concentrate, reprecipitate the hydroxide from dilute sulphuric acid in a very small volume of solution, and add the filtrate to the main solution. Reprecipitate the hydroxide once more from dilute sulphuric acid, filter, wash thoroughly, and add the filtrate to the main solution. Make acid with dilute sulphuric acid and add 2 to 3 c.c. of nitric acid (d., 1.42). Deposit the copper as in the method for electrolytic and low-resistance lake copper.

¹ Guess, *Trans. A. I. M. E.* **36**, 605 (1905).

² Keller, *Ibid. Bull.* **80**, 2099 (1913); Heath, *J. Ind. Eng. Chem.* **3**, 75.

³ Heath (Senter modified), *J. Am. Chem. Soc.* **26**, 1123 (1904).

*Modification III.*¹—(For copper containing only traces of antimony or bismuth but sufficient selenium or tellurium to interfere.)

Dissolve the 5-gram sample in 40 c.c. of "assay solution" and evaporate until fumes appear, or until the residue is white. Redissolve in 60 c.c. of water and saturate the boiling solution for ten minutes with sulphur dioxide gas, removing the solution from the lamp when the gas is started. The gas may be generated by dropping cold saturated sodium sulphite solution into strong sulphuric acid. It is also conveniently obtainable in cylinders. Let the precipitate settle for a few hours, filter, and wash with a little hot water. Boil the filtrate gently to remove most of the sulphur dioxide gas. Ignite the filter in a porcelain crucible to volatilize the selenium and tellurium, redissolve the oxidized residue in 1.5 to 2 c.c. of nitric acid and add to the main solution. Deposit the copper as in the method for electrolytic and pure lake copper.

NOTE.—The selenium is said to be carried down by sulphur dioxide as a selenide of silver, but the roasting sufficiently removes the elements selenium and tellurium. When silver is to be removed, the selenium, etc., are thrown down with the silver by the sulphur dioxide gas and the precipitation is then completed by the addition of chlorides or hydrochloric acid.

Modification IV.—(For copper high in arsenic only.²) The committee gives preference to *B*.

A.—Dissolve the sample in 40 to 42 c.c. of the "assay solution" in the regular way and add 5 grams of ammonium nitrate. Electrolyze as usual.

B.—Dissolve the sample in 60 to 66 c.c. of the "assay solution" instead of 40 c.c. Electrolyze in the usual manner.

3. Notes on the Manipulation of the Frary Solenoid.—This rotary device of Professor F. C. Frary³ produces rotation of the electrolyte in the tall assay beaker by the action of a magnetic field. The apparatus has been described and illustrated in Chapter I.

¹ Heath, *J. Am. Chem. Soc.* **26**, 1123 (1914); Keller, *Trans. A. I. M. E., Bull.* **80**, 2098 (1913).

² Heath, *J. Am. Chem. Soc.* **26**, 1124; *J. Ind. and Eng. Chem.* **3**, 75 (1911).

³ *J. Am. Chem. Soc.* **17**, 395; *Z. Elektrochem.* **23**, 358.

This apparatus makes it possible to obtain results in three hours, or even less, if a circulation of cold water is introduced between the beaker and copper cylinder. There are two objections to rapid deposition of copper which have been alluded to:—the liability to slight oxidation unless the cathode is withdrawn within five minutes after the deposition of copper is complete; second, a trace of platinum is carried over from the anode in warm solutions. It may be removed, as already directed, by filtering the solution of the cathode deposit through paper and igniting the platinum residue, which may amount to .005 per cent. The amount of "assay solution" should not exceed 50 c.c. if the solution is allowed to heat. A perfect assay may always be obtained with 50 c.c. of "assay solution" if the electrolyte is kept *very* cold by water circulation. With 5 grams of copper, the current may be raised to 4 or 4.5 amperes. In about two hours, or just as soon as the liquid becomes colorless, wash down the covers and beaker, and twenty minutes later begin to make tests once in five minutes upon test portions of 1 c.c. of the electrolyte. As soon as a negative test is obtained, withdraw the cathode very rapidly with one motion and plunge it into a beaker of cold water. Wash, ignite, and weigh as usual. The perforated cathode of Andrews and Keller (method 1) should be employed.

In the case of casting copper, if the first deposit is slightly impure, it may be redissolved in diluted stock solution and replated. The use of 50 c.c., or more, of "assay solution" will prevent sponginess and no platinum will be dissolved, if the electrolyte is kept very cold as recommended.

CHAPTER XII

THE DETERMINATION OF FOREIGN ELEMENTS IN COPPER

Division of Work.—Metallurgical chemists usually consider that it is more rapid and accurate to make special determinations of single elements or groups upon separate portions of copper drillings from the same casting. In addition to the electrolytic assays described in Chapter XI, it is customary to weigh out a second sample of 50 grams for electrolysis followed by separation of iron, nickel, cobalt, and zinc; also a third sample of 25 to 100 grams for the separation of the arsenic or selenium groups of metals. A fourth sample weight of 20 grams is taken for sulphur and lead determinations; occasionally a fifth for a check on bismuth, and a sixth of 50 grams for the estimation of oxygen. It is reasonably correct to determine the known impurities in commercial copper, subtract their sum from 100 per cent, and take the difference as oxygen. A sample for oxygen test should be weighed out from the same bottle of drillings as the sample for battery assay, because the oxygen increases nearly as much as the copper decreases. A single casting shows much segregation in this respect.

As it is occasionally necessary to examine a small piece of metal, two general schemes are presented in methods 1, 2, 3, 4, and 5,¹ by which most of the impurities are removed from a single solution. Although adapted to some routine work, these older methods (1, 2, 4, 5), which are modifications of the original process of Dr. W. Hampe,² are not so accurate for the estimation of minute amounts as the special methods which follow them.

1. Foreign Metals (*with Separation of Copper as Thiocyanate*).³—Transfer 50 grams of pure copper or 25 grams of "casting" copper to a 750 c.c. beaker. Twenty-five grams of metal require for solution 125 c.c. distilled water, 35 to 40 c.c. pure sul-

¹ *J. Am. Chem. Soc.* **29**, 699; **27**, 317.

² *Z. Berg. Hutten und Salinen-Wesen* **21**, 218; **22**, 93; also Fresenius' *Zeitsch.* 1874.

³ *J. Am. Chem. Soc.* **16**, 785.

phuric acid (d., 1.84), and 28 to 30 c.c. of nitric acid (d., 1.42). For a 50-gram sample double the reagents but add the nitric acid in three portions. Dissolve by heating, dilute with an equal volume of water, heat to 40° C., and pass sulphur dioxide until the liquid is saturated with the gas. If an accurate separation of selenium or tellurium is required, the original solution should be evaporated to dryness to remove all nitric acid, before dilution and reduction with sulphur dioxide. One or two drops of hydrochloric acid may be added to complete the deposition of the silver. After standing over night in a warm place (below 40° C.), pour off the supernatant liquid through a small filter into a calibrated 2-liter flask. The sediment, after washing out the last trace of copper, may contain gold, silver as metal and chloride, selenium, tellurium, possibly also lead sulphate and traces of antimony and bismuth.

Dilute to one liter or more and remove the copper by adding gradually a standard solution of ammonium (or potassium) thiocyanate, while a current of sulphur dioxide is conducted into the bottom of the flask through a long tube or pipette. Give the flask a vigorous rotation before each addition of reagent until the precipitate changes to the white salt. A sufficient amount of copper should finally remain to impart a faint tint to the solution. Withdraw the delivery tube, fill the flask with water to the mark, and mix the contents thoroughly by pouring several times into a large dry beaker. Allow the mass to settle, filter off a known portion, say 1800 to 1900 c.c. for analysis, and expel the sulphur dioxide by heating. It is necessary to allow for the volume of the thiocyanate, the specific gravity of which is nearly three (Hampe). Twenty-five grams of copper give 48 grams of the salt, hence the volume of the salt is 16 c.c. and the volume of the solution in the flask at the filling mark is not 2000 but 1984 c.c. Similarly, the volume of the solution from a 50-gram sample is 1968 c.c. The determination of iron by this method is not very certain on account of the variable trace of iron in the large amount of thiocyanate required.

Analysis of Insoluble Residue. — Remove the residue as completely as possible from the filter and destroy the latter by repeated gentle evaporation with a little red fuming nitric acid in a small porcelain casserole. Add the residue and treat again with nitric acid until completely oxidized. After the acid is

finally removed by evaporation on the steam bath, digest the dried residue with dilute hydrochloric acid, which leaves the silver chloride undissolved. If a trace of antimony is suspected, digest the silver chloride with 20 c.c. of a saturated solution of yellow ammonium sulphide, containing .5 gram of ammonium chloride, in order to dissolve the antimony. Preserve this extract and afterwards unite it with the remainder of the antimony obtained from the main solution. Oxidize the sulphides with nitric acid, evaporate to dryness, add dilute hydrochloric acid in sufficient amount to dissolve the salts and separate the silver; then filter. If silver alone is required, it is possible to char and oxidize the sulphides direct upon a Brownite cupel, cover with powdered lead, and finish the cupellation. If silver chloride is to be weighed, it is best to filter it upon a dried asbestos felt in a Gooch crucible, and dry at 150° C.

Precipitate the selenium and tellurium in the acid filtrate from the silver chloride by sulphur dioxide in excess. If a separation of the two elements is required, evaporate the solution to 10 c.c. or to 5 c.c. if possible, and then add strong hydrochloric acid (d., 1.2), until the acid is 90 per cent strength. Heat nearly to boiling to reduce selenium, charge with sulphur dioxide until cold, and allow to settle.

Filter off the selenium upon an asbestos felt which has been washed in strong acid and water, dried, and weighed. Then proceed to wash, dry, and weigh the selenium. Separate the tellurium in the filtrate according to special method 16, Chapter XIII. Lead is also determined by a special electrolytic method, given in the next chapter. Hydroxyl amine will throw down selenium but has little effect on tellurium.

Analysis of the Main Solution.—Expel the sulphur dioxide by heat, then charge the solution with hydrogen sulphide until saturated, to precipitate the arsenic group of metals and the remaining traces of copper. Extract the arsenic, antimony, and tin by digestion of the sulphides with sodium (or potassium) sulphide as directed in 4. Charge the original solution with hydrogen sulphide again, and filter to prove that the first precipitation was complete. Repeat the treatment if more than a trace of sulphide appears after all sulphur has been extracted with ethyl alcohol and carbon bisulphide.

Owing to the presence of an excessive quantity of salts, the iron, nickel, and zinc are subsequently removed from the main solution by rendering the liquid slightly alkaline with ammonia and recharging with hydrogen sulphide. Filter off the sulphides, and repeat the process as often as necessary. Dissolve the sulphides by heating with dilute hydrochloric acid, adding a little nitric acid, if much nickel and cobalt are present. Precipitate the iron twice with ammonia from the oxidized solution. If a trace of manganese is present, add some bromine water during the first precipitation. When the iron is to be purified a second time, the manganese may be taken out of the ferric precipitate by omitting the bromine and using considerable hydrochloric acid and ammonia, or by making a small "basic acetate" separation.

The filtrate from the iron contains the cobalt, nickel, and zinc. These may be determined by method 1, Chapter XIII. The process, just described, is rather slow and requires much manipulation, but is capable of giving exact results for all impurities in copper except gold, iron, and lead.

ELECTROLYTIC SEPARATIONS

2. Arsenic, Antimony, and Tin in Crude Copper.—The original methods¹ have been modified and improved by Heberlein, Heath, and Brownson,² in order to adapt them to rapid routine work. Electrolytic separations, however, cannot be considered as reliable as methods 6, 7, 8, in which the arsenic group is separated from the bulk of the copper by a special precipitant. It is never safe to assume that the first cathode from casting, or converter, metal is absolutely pure. The first cathode should be redissolved in nitric acid, or diluted "acid mixture," and the solution electrolyzed a second time, until the copper is entirely removed.

(a) *Arsenical Lake Copper.*—With metal containing .05 to .1 per cent of arsenic, 10 grams of drillings may be dissolved in 70 c.c. of "assay solution" and the solution electrolyzed for copper as described in method 2, Chapter XI. When the metal contains only .05 per cent arsenic, two electrolytes may be combined, the washings added, and the whole solution treated for arsenic. For metal containing more than .05 per cent

¹ *Trans. A. I. M. E.* **27**, 962.

² *A. I. M. E. Bull.* **80** (1913), 1489.

arsenic, methods 6 and 7 are more accurate. (It is easy to lose a little arsenic, partly by volatilization, partly by deposition on the copper if the current is not interrupted at the right time.) When the arsenic is well oxidized and such loss is avoided, the electrolytic method may show .005 per cent higher results for arsenic than other methods, unless one can eliminate, before titration, a trace of platinum which may be carried into solution from the anode. This platinum may be partially removed by fractional precipitation with hydrogen sulphide water. Combine the electrolyte and washings, remove the nitric acid by a second evaporation to dryness, dilute to 150 c.c., add to the hot liquid 1 c.c. of strong hydrogen sulphide water, and filter after five minutes. Repeat the operation as long as a brown tint is formed at once without any yellow precipitate.

Then proceed to the separation of the arsenic according to method 6b.

(b) *Rapid Method.* — An approximate assay of refined arsenical copper, free from antimony, may be quickly obtained by direct reduction and titration of the electrolyte from which the copper has been removed. Transfer the electrolytes to a 500 c.c. beaker, add 3 grams of potassium bisulphate, and evaporate on the hot plate until fumes of sulphur trioxide have been evolved for five minutes.

Cool the liquid, wash it into a long-necked Kjehldahl flask of Jena glass, place the flask in an inclined position over a small flame, and boil off the water. Allow to fume for five minutes again, and when the time is nearly up, flash the neck of the flask with another lamp flame long enough to drive out any trace of nitric or sulphuric acid which may have condensed. This double fuming process is the secret of success with the method of reduction to be described. After the flask has partly cooled, add from a paper .5 gram of coarsely powdered tartaric acid and digest until the solution becomes colorless, giving the flask an occasional whirling motion. Allow to cool, wash into a 400 c.c. beaker, and fill the beaker about half full of water. Drop a small piece of litmus paper into the beaker, add ammonia until the liquid is just alkaline, and then make the solution acid with sulphuric acid, adding only one drop in excess. Several such digestions may be conducted at once. Place the beakers in a pan of water to cool, then carefully neutralize each solution with

8 to 10 grams of pure sodium bicarbonate. Add 5 drops of a 10 per cent solution of potassium iodide, 3 c.c. of starch solution, and titrate with iodine as in method 6. A blank test should be made with each new lot of reagents, and the iodine reading of about .2 c.c. deducted from each burette reading obtained in the analyses.

3. Rapid Electrolytic Method for Arsenic and Antimony in Anodes. — The direct reduction and titration of an electrolyte (method 2b) is only intended for rough work. The following separation of E. E. Brownson is more accurate, although less reliable than the distillation and reduction methods 6, 7, 8. Treat 10 grams of the sample in a 750 c.c. beaker with 30 c.c. of sulphuric acid, 20 c.c. of nitric acid, and 50 c.c. of water. Drive off red fumes, add water until two-thirds full, and electrolyze about two and a half hours at 4 amperes. The metal may be deposited on a large platinum gauze cylinder having the following dimensions: height, 7.5 cm.; diameter, 7.5 cm. The gauze is made of wire .22 mm. in diameter with 36 meshes to the inch (or 14 per cm.) and is strengthened by rings. The deposition is continued until the solution contains about .25 gram of copper. It then has a faint blue color. The cathode is rinsed with a jet when removed from the solution. The acids are now neutralized with ammonia and the solution made acid with hydrochloric acid, adding 2 or 3 c.c. in excess. Pass a rapid stream of hydrogen sulphide for about 30 minutes and allow to settle for about 30 minutes. Filter through a 12.5 cm. paper (C. S. & S.) in a 7.5 cm. funnel, discarding the filtrate. Wash once on the paper with water and then wash the sulphides into a No. 3 (or tall No. 5) beaker with the smallest possible amount of water. Place the beaker containing the sulphides under the funnel and dissolve any sulphides still adhering to the filter with 25 to 30 c.c. of hot aqua-regia poured carefully around the edges of the paper. It is usually well to pour about 10 c.c. of the aqua-regia into the original beaker and transfer from it to the paper, as sometimes a film of antimony forms on the bottom of the first beaker. To prevent destruction of paper the acid may be diluted one-fourth with water, although the whole must be very hot to attack the sulphides. Wash the No. 5 beaker and paper with a small amount of water only, as extra solution above that consistent with good work means extra time for

evaporation. Cover the beaker, boil about 30 minutes to break up sulphides and remove the cover, washing beaker, and cover with a fine jet. Continue the evaporation to complete dryness, at a temperature just high enough not to cause loss by spattering, and heat until the residue has no acid odor.

Add about 4 or 5 grams of potassium hydroxide, 30 c.c. of water, and boil vigorously for 10 to 15 minutes. All arsenic and antimony will go into solution. Add 25 c.c. of strong sodium sulphide solution (450 grams of fresh monosulphide crystals in 2 liters of water), and boil vigorously for 5 or 10 minutes. Allow to cool, decant the clear liquid through an 11 cm. paper (C. S. & S. 597) into a 250 c.c. beaker, again add 25 c.c. of the strong sodium sulphide solution to the black sulphide in the beaker, stir well and filter off, washing well with a jet of dilute sodium sulphide (450 grams to 8 liters). If the mass is kept very wet to prevent oxidation of copper sulphide, hot water may be used instead. Add 5 c.c. of strong hydrogen peroxide to the diluted filtrate (volume 150 to 175 c.c.), and heat until the strong yellow color fades. Unless too much organic matter has been dissolved from the paper, the liquid should become nearly colorless.

Antimony.—Cool the liquid and electrolyze over night at from .10 to .15 ampere per square decimeter of cathode surface. Antimony alone is precipitated. In the morning, remove the cathode with a very rapid motion and carefully wash the adhering solution into a clean 500 c.c. beaker with a jet of water. Wash the deposit in water and two changes of alcohol, dry carefully over an alcohol flame, and weigh the antimony. The best cathode is an ordinary split foil which has been roughened by long use.

Arsenic.—Transfer the solution entirely to the 500 c.c. beaker and make distinctly acid, using dilute sulphuric acid (1 part to 4 of water). Pass a strong current of hydrogen sulphide for about ten minutes, allow to settle for twenty to twenty-five minutes, and filter through an 11 cm. paper, which will retain the arsenic but not the finely divided sulphur. It is best to decant the clear liquid, only, through the paper, then transfer the heavy sulphide and sulphur with remaining solution directly to a 200 c.c. beaker by a jet of water. Now decant any excess of water from the No. 2 beaker through the paper and place this

No. 2 beaker and contents under the funnel. Dissolve the small amount of arsenic on the paper into the beaker with dilute ammonia (1 to 4 of water). It is best to wash down the sides of the 500 c.c. beaker with 10 to 15 c.c. of this dilute ammonia in order to recover any adhering arsenic. Then pour this washing around the edges of the filter, wash the large beaker with the jet, and allow all the washings to run into the small beaker.

Make the contents of the beaker acid with sulphuric acid and add 7 or 8 c.c. in excess. Evaporate to fumes of sulphur trioxide at a temperature just high enough not to cause loss by spattering, and then raise to a very high heat for one hour to an hour and a half. Cool, wash the rim and the sides of the beaker very thoroughly with water, add water to half fill the beaker, neutralize the acid with ammonia, make slightly but distinctly acid with hydrochloric acid, and filter through an 11 cm. paper into a 500 c.c. beaker, washing well with hot water. Add water to half fill this beaker, neutralize the acid with sodium bicarbonate, and add 3 or 4 grams in excess. Cool to room temperature and titrate with iodine. Solution 21 of Chapter III may be employed. The author quoted prefers to dissolve 5.105 grams of "reagent" iodine in a little water with 8.5 grams of potassium iodide and dilute to one liter. Then 1 c.c. equals .0015 gram arsenic. The next method is another variation of the electrolytic separation.

4. Electrolytic Separation of Foreign Metals from Mansfeld Copper.¹—Twenty grams of sample are dissolved in a beaker (10×17 cm.) with 160 c.c. of nitric acid (d., 1.2); the solution diluted to 1 liter and electrolyzed after the addition of 20 c.c. of sulphuric acid (d., 1.2). A platinum cylinder, 6 cm. \times 10 cm., is used as a cathode with a spiral anode; current, 1 ampere at 2.3 volts tension across the terminals; and time, twenty-four to thirty hours. Dr. Toisten of the same Company uses a gauze cathode with an anode revolving at 500 to 600 revolutions per minute, then separates the arsenic from the remaining liquid and distills it (according to E. Fischer-Hufschmidt-Classen).

H. Koch estimates arsenic in a special sample, but determines the antimony, with any tin present, by the following treatment of the electrolyte from which the copper has been removed.—

¹ Hermann Koch, personal communication.

Wash off the cathodes of copper and concentrate the liquid to fumes of sulphur trioxide. Take up the residue in water with 25 to 30 c.c. of hydrochloric acid (d., 1.2) and warm; then transfer the clear solution to a beaker and treat with hydrogen sulphide in excess. Filter, and wash the sulphides with hydrogen sulphide water. Evaporate the main solution to fumes with the addition of a little nitric acid, and determine iron, nickel, and zinc by the methods described in Chapter XIII.

To recover antimony (and tin if present), the sulphides are dissolved in the original beaker at a gentle heat by treatment with 30 c.c. of ammonium sulphide. The paper and copper sulphide are washed with ammonium sulphide water, and the antimony, in solution, deposited in a 250 c.c. beaker on a platinum cylinder of 66 sq. cm. total surface. With a current of .5 ampere, .05 gram may be deposited in three to four hours, while arsenic remains in solution.

It should be observed that antimony deposits alone from solution in sodium sulphide (methods 3, 5); while antimony and tin precipitate together from ammonium sulphide. Electrolytic separations from alkaline sulphides are more suited to considerable amounts of the elements deposited. Compare this with the electrolysis (10) in acid ammonium oxalate in which an accurate deposition of pure tin is obtained.

5. Electrolytic Separation of Antimony from Tin.—In the preceding methods a little trouble is sometimes experienced from

ANTIMONY FROM TIN

Rev. per m.	Weight Anti- mony	Vol. cc.	Reagents in Electrolyte	Amp.	Cathode Density	Volt- age	Temp. °C.	Time Min.	May be separated from—
300– 400.	.05 to .10 g.	120. ..	80 g. Na_2S cryst. 6.5 g. KCN. 2. g. KOH.	.5 to 1	1.75	1.1 to .9	60– 50.	40– 50.	0.5 to .6 g. of tin as chlo- ride

the deposition of a trace of sulphur with the antimony. The formula for the electrolyte in this alternative method was devised by Dr. Toisten as an improvement on the original method of Classen. Proceed as in 3 or 4, using hot sodium sulphide as the agent of extraction; then bring the solution to

the conditions of density, temperature, and volume noted in the table. Wash the deposit with water and alcohol, dry at 105° C., and weigh.

SPECIAL METHODS FOR ARSENIC, ANTIMONY, AND TIN IN REFINED COPPER

6. By Precipitation with Ferric Hydroxide and Ammonia. — In its present form, this separation has been developed by A. M. Smoot and F. D. Greenwood, with modifications by W. H. Bassett and Alden Merrill. In the combination method **7** the author makes use of the same principle. Ferric hydroxide, when precipitated from a copper solution by a slight excess of ammonia, forms insoluble compounds with any arsenic and antimony present, if they have been oxidized to the pentavalent condition during the solution of the copper. The compounds of lower oxidation are relatively more soluble.

Method. — Dissolve 25 to 50 grams of "casting" copper in a liter beaker in 100 or 200 c.c. of nitric acid (d., 1.42). Boil off the red fumes and evaporate off acid for fifteen minutes by letting the solutions stand without cover-glasses in the center of the hot plate. Dilute to 300 c.c. and the liquid will be ready for the iron treatment.

To analyze "high-grade" metal, treat 100 grams in an 1800 c.c. beaker with 400 c.c. of nitric acid (d., 1.42). Take the solution off the hot plate and let it cool; add cold water to make the volume 500 c.c. Neutralize with ammonium hydroxide until just enough copper hydroxide has formed to sparsely cover the bottom of the beaker; then add about 5 grams of crystallized ferric ammonium sulphate in aqueous solution and add hot water to the beaker until the volume is about 1000 c.c. for a 100-gram sample (or 500 c.c. for 50 grams of copper). For a 100-gram sample of wire-bar copper, A. M. Smoot recommends .5 gram of ferrous sulphate crystals, but results will be more trustworthy if 2 grams are used. As a general rule, the iron should be at least 10 times the weight of the arsenic and antimony, or 20 times that of the selenium and tellurium, if the latter are to be precipitated with the arsenic, as in **7**.

Boil the solution for one half-hour, remove from the plate, and add cold water until the volume is about 1500 c.c. for a 100-gram sample. Allow to settle for a period of one to five

hours; that is, until a trial proves that the liquid will yield a clear filtrate. Filter on a 15 cm. paper supported by a platinum cone, wash the precipitate several times with hot water until nearly all the soluble copper is washed out. It is possible to neutralize the solution with ammonia just far enough to provide a slight excess, only, beyond the amount necessary to react with the ferric sulphate on boiling. A very little basic copper should remain in the washed precipitate, or a little iron may be held in solution with resultant loss of a trace of antimony. In the analysis of any material containing more than .002 per cent of arsenic, the author adds one gram of the ferric salt to the clear filtrate. A few drops of ammonia should then be added until a slight precipitate appears, the solution heated to boiling, settled for a short time, and again filtered, but on a separate paper. All nitrates must be removed from the ferric hydroxide, generally by re-precipitation.

If bismuth is present, a drop of hydrochloric acid and a little ammonium carbonate may be added during the precipitation, using such an excess of ammonia that .2 to .3 gram of copper will be rendered basic. This copper salt is afterwards removed by dissolving the precipitate in a little dilute nitric acid, and re-precipitating with a considerable excess of ammonia to dissolve the basic salt of copper. Although arsenic may be separated from antimony and tin by gravimetric methods (9, 10), the distillation of the arsenic as arsenious chloride is the most rapid separation, and may be made very accurate by the observance of certain conditions. As contributors have given no adequate explanation of the conditions necessary for the complete reduction and evolution of the arsenious chloride, a personal study has been made. The most important ingredient, besides hydrochloric acid, which should be present in the distilling flask, is a salt of copper, in amount equivalent to about .5 gram of the crystallized cuprous chloride. In the absence of this metal, the evolution of arsenic is apt to be very incomplete. In the distillation of arsenic from solutions of ores and mattes, the saturated double chloride of copper and zinc is employed. See method 6, Chapter VI.

Since acids may contain traces of arsenic, the proper acid to use in distillation is the pure hydrochloric acid now made by the electrolytic process. A careful blank analysis and distillation

should be carried through, and the still should not be allowed to cool, until the last addition of acid and distillation has been completed. If the flask cools and the stopper is washed down by fresh acid, a little more iodine would be required, in subsequent titration of the distillate, due to increased action on the rubber stoppers.

Three successive distillations are generally necessary to remove every trace of arsenic from the flask, and in the last two, a reducing agent is introduced, which reduces both iron and arsenic to the lower chlorides. Ferrous chloride or sulphate was formerly employed; the latest and most effective substance is hypophosphorous acid, which should not be added in too great excess at first or arsenic may be reduced to the black metallic condition. In presence of selenium, tellurium, or much antimony, the distillation should be made with chlorides free from sulphuric acid.

ARSENIC

6a. Distillation of Arsenic with Hypophosphorous Acid as Reducing Agent. — The ferric hydroxide precipitate, produced in the treatment of the copper solution, is dissolved in warm hydrochloric acid (15 to 25 parts to 75 of water). Transfer the solution with the aid of a little strong hydrochloric acid to a 300 c.c. Erlenmeyer flask, through a 60 c.c. glass-stoppered separatory funnel. The delivery tube is bent into inverted U form, and filed at a sharp angle on each end to prevent any chloride of iron from being carried over mechanically. The flask is connected by the delivery tube and black rubber stoppers to the top of a vertical 8-inch (20 cm.) Allihn condenser, the lower end of which is just sealed by 150 c.c. of water contained in a 400 c.c. beaker. A few glass beads in the flask will prevent bumping during distillation. (See Fig. 15.)

The covered beaker may be supported on an adjustable ring. By lowering this gradually as the distillations progress, the seal is preserved, but the solution can never rise any higher than the first bulb of the condenser without breaking the seal. Reverse suction is thus avoided. With this precaution, a dozen stills may be run by one operator. The total amount of hydrochloric acid in the still should be 50 c.c. As the ferric hydroxide was reprecipitated and the copper removed in the ammonia treatment, .5 gram of cuprous chloride should be added to

the flask before the solution is introduced. Distill until the volume is reduced to about 20 c.c. (One operator distills for a half-hour longer, adding concentrated hydrochloric acid to replace that which distills over.) To be sure of the complete evolution of arsenic from any sample, add 30 c.c. of strong hydrochloric acid to the residue from the first distillation without cooling the flask, and follow with .5 c.c. of 50 per cent hypophosphorous acid. Distill down again to about 20 c.c. Without cooling, add 30 c.c. more strong hydrochloric acid with .5 c.c. of the 50% hypophosphorous acid and distill a third time. If any doubt exists as to the completeness of the evolution, another distillation with more acid may be continued for fifteen minutes, and the distillate collected in a separate beaker, and treated by itself.

6b. — Distillation with Ferrous Salt as Reducing Agent. —

In this older method, the ferric hydroxide is dissolved in 3 to 10 c.c. of sulphuric acid diluted with 5 parts of water and transferred to the Erlenmeyer, or round-bottomed Jena flask. Smoot prefers to add enough acid to make the total amount 5 to 6 c.c. for high-grade copper samples, then evaporate to fumes by shaking the flask over a naked Bunsen flame and directing a gentle current of air into the flask. The flask is then cooled, and 2 c.c. of water and 2 grams of ferrous sulphate are added. Connect with the Allihn condenser, add 60 c.c. of strong hydrochloric acid and distill down to about 25 c.c., then add 40 c.c. more of strong hydrochloric acid and distill again to a volume of 25 c.c. Some operators now prefer to remove the distillate,

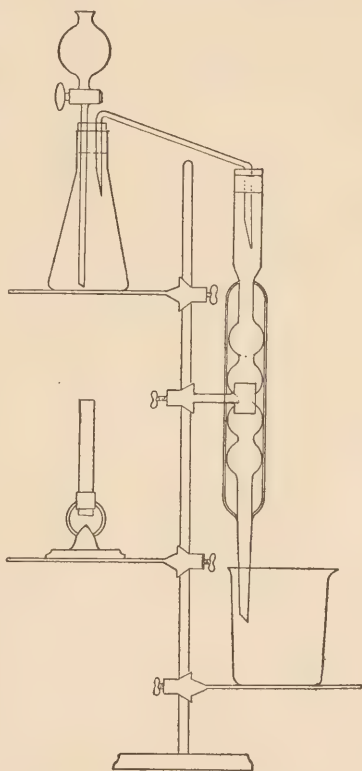


Fig. 15. — Distillation Apparatus.

add 40 c.c. more acid, repeat, and test the last distillate by itself. With miscellaneous samples, there is no advantage in separating the distillates. If the last distillate does not show any more test by titration with iodine than would be obtained by distilling 40 c.c. of acid with pure copper salt and reducer, the operation is finished. When the distillate is titrated with iodine, a slight blank will be obtained from the purest hydrochloric acid, due to its action on the rubber stoppers. As already stated, this distillation from a solution, which at the end contains very strong boiling sulphuric acid, is rather uncertain in presence of selenium and tellurium, which are somewhat volatile under the conditions specified. Chloride of antimony begins to volatilize at 120–122° C., and the temperature of the liquid in the flask should not rise above 118°.

With the hydrochloric acid and chlorides (a), arsenic has been separated by distillation from .01 gram of selenium and tellurium.

If sulphuric acid is distilled too far, in presence of the first reducer described (a), it may be slightly decomposed, thus injuring the distillate.

6c. Treatment of the Distillate by Hydrogen Sulphide.—

To finish the analysis by the slower gravimetric modification, proceed to charge the cold or slightly warm solution with hydrogen sulphide, until it smells strongly of the gas. Allow to settle and filter the yellow arsenious sulphide on a weighed Gooch crucible which has been made up with a paper disc and acid-washed asbestos, and dried at 100° C. before weighing. Extract the yellow salt with alcohol followed by carbon bisulphide. Wash finally with alcohol and ether and dry in an oven at 100° C., or less. The principal objection to this modification is the difficulty experienced in extracting every trace of sulphur by volatile solvents.

6d. Titration of Arsenious Acid by Iodine.— Distillates, containing no more than traces of arsenious compounds, may be titrated with a definite and sharp end-point, if a little ammonium sulphate is present at the time of titration, and if 4 or 5 drops of a 10 per cent solution of potassium iodide are added to the distillate after it has been completely neutralized with a large excess of sodium bicarbonate.

To prepare a solution for titration, dilute the clear liquid resulting from the digestion prescribed in the next method (7),

or the hydrochloric acid distillate from the preceding (6), until the volume is about 200 c.c. Neutralize with strong ammonia, using a floating piece of litmus paper as an indicator. If the solution becomes very warm, cool it during neutralization by standing the beaker in a large pan of cold water. Bring the liquid back to a slightly acid reaction by a few drops of dilute sulphuric acid. To the cold, faintly acid solution, add gradually 8 to 10 grams of pure sodium bicarbonate, keeping the beaker covered. Wash off the cover, add 4 to 5 drops of the potassium iodide, 3 c.c. of starch indicator (57, Chapter III), and titrate with the standard iodine, one cubic centimeter of which oxidizes about .001 gram of arsenic (As). Refer to solution 21, Chapter III.

To standardize the iodine, dissolve weighed portions of .06 gram of chemically pure arsenious oxide in a little water with the aid of .5 to 1 gram of potassium hydroxide. Transfer the solution to a 400 c.c. beaker, dilute to 300 c.c., make slightly acid with sulphuric acid, then alkaline, then faintly acid. Treat with the excess of sodium bicarbonate, followed by the trace of potassium iodide and starch, and titrate with the iodine. Correct for the slight excess of about .04 c.c., required to produce the change of color from red to a purplish blue. The temperature of the iodine should be noted at the time of standardization, and correction made to analyses of high-grade copper, for any appreciable variation of temperature. As the iodine solution is a little viscous, a specified time should be allowed for the draining of the burette, — say, five minutes for 50 c.c. of reagent.

Careful blank analyses should be made with the reagents under the same conditions.

7. Combination Method (including Selenium and Tellurium).¹

— The separation is nearly the same as that of the preceding method, but an excess of ammonia is employed great enough to precipitate all the copper as hydroxide and to redissolve it to a clear solution of the complex salt. Other reagents are added to complete the separation of antimony, bismuth, selenium, and tellurium.

If the metal contains less than .05 per cent of arsenic, 50 to 100 grams of copper are taken for each analysis. This quantity is reduced to 25 grams with arsenical copper. For 50 grams of copper

¹ By author.

add gradually 210 c.c. of nitric acid (d., 1.42), dilute the solution with water until the 1500 c.c. beaker is half full, and introduce 5 grams of ferric ammonium sulphate, or an equivalent amount of ferric sulphate. Heat nearly to boiling, add strong ammonia until the basic hydroxide of copper has formed and redissolved. This requires about 300 c.c. If bismuth and antimony are to be determined, add (after the ammonia) 2 grams of ammonium carbonate and 5 c.c. of saturated solution of sodium phosphate. Bring to a boil, allow to settle for an hour on the steam plate, and filter quickly through a 15 cm. washed filter, supported by a platinum cone with coarse perforations. Keep the solutions warm to prevent crystallization, and wash the blue color out of the filter with dilute (1 to 20) ammonium hydroxide. Pass the filtrate through a second filter to recover traces of iron which may pass the first paper.

If the copper contains more than .005 per cent of arsenic, the filtrate should be treated a second time with iron and ammonia, using, however, just enough iron salt to clean the solution. Make the first filtrate and washings acid with nitric acid, add .5 gram of oxidized ferrous sulphate, or 1 gram of the alum, and sufficient ammonia to complete the precipitation as before. Allow to settle and filter. Preserve this hydroxide separately. Wash the large precipitate of ferric hydroxide into a 400 c.c. beaker and dissolve that which remains on the paper with a little hot dilute sulphuric acid. Wash the filter with a little ammonia, then precipitate the ferric hydroxide with ammonia, ammonium carbonate and phosphate, filtering on the original paper. Wash out the copper salts. Clean this last filtrate from any trace of arsenic, etc., by adding to it the solution of the small precipitate of ferric hydroxide, which was reserved.

Make acid, then precipitate again with ammonia, filter, and wash. The ferric hydroxide may now be redissolved in 40% hydrochloric acid and the arsenic distilled as in 6a. In presence of much selenium or tellurium proceed as follows:—

Separation of Selenium and Tellurium.—Transfer all the iron precipitates to a 500 c.c. beaker, and dissolve any precipitate adhering to the papers by repeated treatment with a little hot dilute sulphuric acid. Record the amount of all acids used in order to make a blank test of the reagents.

To remove the last traces of bismuth, or antimony, from the

filters, boil the papers with a little 25 per cent hydrochloric acid. Nitric acid of 15 per cent strength will extract bismuth. Preserve this extract as "solution B" until the selenium and tellurium have been separated from the sulphuric acid solution of the ferric hydroxide. The following separation is successful as outlined, only when hydrochloric acid is not present. For chloride solutions, use Keller's method 17 (Chapter XIII).

Heat the sulphate solution to boiling and saturate it with a rapid current of sulphur dioxide, generated as described in Chapter III. Continue charging for one hour at 80 to 85° C., or until the precipitate has formed, and allow to partially cool while passing the gas. Settle over-night on the work-table, and filter the liquid through an asbestos felt in a Gooch crucible. If the selenium is to be separated from the tellurium, the first felt need not be weighed. For weighing, prepare a felt with acid-washed and ignited asbestos, and take the weight of ignited felt. Then moisten the felt with a little water, dry in an oven for one hour at 105° C., and weigh to obtain the "dried weight." Dry the washed precipitate of selenium and tellurium in the same way, and deduct from the final weight the "dried weight" of the pad. As a check, the weighed felt may finally be ignited at a red heat, cooled and reweighed, using as a tare the original "ignited weight" of the pad. Repeat the treatment of the solution with sulphur dioxide as before and weigh any additional selenium and tellurium. No more than a trace should appear. For the separation of the two elements, refer to the special method 17, Chapter XIII.

Arsenic and Antimony.—The small "solution B" should now be added to the principal solution of ferric salt and the sulphur dioxide expelled by boiling. Pass a rapid current of hydrogen sulphide through the warm solution for fifteen minutes and allow to stand until the sulphides appear granular. Then charge again with the same gas and allow to settle over-night. In the morning, treat with hydrogen sulphide again until the liquid smells strong, filter, and remove the sulphide from the beaker with the aid of bits of paper and stiff platinum wire. Transfer the paper and contents to a 75 c.c. beaker. Heat the main solution to 85° C. and saturate with hydrogen sulphide, settle, filter, and repeat this treatment as long as a trace of yellow sulphide remains on the filter after extraction with alcohol and carbon bisulphide.

Separation of Arsenic from the Antimony and Tin.—The sulphides may be transferred directly to the distilling flask described in the previous method, and the arsenic directly distilled off with a special distilling solution according to method 1, Chapter VI. Precipitate the arsenic as in 6c, or titrate.

The arsenic may be separated **gravimetrically** as follows,—when antimony and bismuth are to be determined: Digest the sulphides in the 100 c.c. beaker on the hot plate with 20 to 30 c.c. of a mixture of sodium monosulphide (d., 1.08) and 2 parts of water. An equal part of potassium sulphide, or hydroxide, should be added to the sodium sulphide when bismuth is present to prevent the solution of a trace of that metal. (A satisfactory extraction for a first treatment may be obtained by using 30 c.c. of a strong solution of yellow ammonium sulphide, containing 1 gram of ammonium chloride. A little copper sulphide may, however, be dissolved, in which case a slight excess of potassium hydroxide may be added before final evaporation.) Filter the liquid through a small paper and wash with the solvent, diluted with ten parts of water. The sulphides of bismuth, lead, and copper remain insoluble. The clear yellow solution is taken to dryness on a steam plate, filtering out any trace of black sulphide which may appear. Treat the residue with 20 c.c. of red, fuming nitric acid (d., 1.60 to 1.70), and digest until the sulphur disappears. Remove the cover and evaporate to dryness.

The next step is to separate pure sulphide of arsenic from a concentrated hydrochloric acid solution.¹ Dissolve the residue in 25 c.c. of water, adding a small crystal of tartaric acid, and, finally, 50 c.c. of hydrochloric acid (d., 1.2). Saturate the cold, or slightly warm, solution with hydrogen sulphide, allow to settle for ten to fifteen minutes only, and filter on an asbestos felt, or paper filter. Wash the sulphide with acid of the same strength, and remove adhering sulphide from the beaker with wads of asbestos, or paper. Remove the flask, or bottle, with the filtrate, then wash out the last traces of acid from the filter with water and reject the washings. Test the filtrate again with hydrogen sulphide, filter, and repeat the treatment if necessary. One precipitation should be sufficient, however.

Preparation of Arsenious Compound for Titration.—The sulphide may be dissolved with a very little dilute sodium (or

¹ G. A. Heberlein, *Trans. A. I. M. E.* **27**, 967.

ammonium) sulphide,—free from chlorides,—the solution washed into a 300 c.c. Kjehldahl flask of Jena glass; the liquid then treated with 25 c.c. of strong sulphuric acid and 3 grams of potassium bisulphate, and evaporated to fumes. It is necessary to boil hard enough to expel every particle of sulphur from the neck of the flask. Add .5 gram of crystals of tartaric acid, rotate the flask, digest until colorless, cool, dilute, and titrate as directed in method **2b**. The operation of digestion in the flask is more rapid, if the sulphur is all destroyed by a preliminary treatment in a covered beaker with fuming nitric acid. Evaporate the clear solution to dryness with 6 drops of sulphuric acid, treat with 25 c.c. of sulphuric acid, evaporate again, and fume for five minutes. Transfer the cooled solution to the digestion flask and proceed as in **2b**, observing the precautions for the removal of all traces of nitric acid.

Any bismuth in the black sulphides, insoluble in alkalis, may be determined by methods 1 or 2, Chapter XIII.

8. Precipitation of Arsenic Acid by Magnesia Mixture.—The original procedure of Fresenius has been modified to secure a more complete precipitation. This is accomplished by reducing the final volume of the solution and washings to the lowest possible limit. This accurate method is only used at present as a check, the more rapid process of distillation and titration having the preference in technical work.

Proceed with the solution of copper according to the sixth or seventh method until the pure arsenious sulphide has been separated. If the copper contains, however, but a trace of antimony and the reagents or distilled water show no trace of tin, it is not necessary to make any preliminary separation of the arsenic from antimony. Evaporate the ammonium sulphide solution of the arsenic and antimony sulphides to dryness on the steam plate, adding .1 to .3 gram of sodium nitrate. Treat the residue (or the pure sulphide obtained in method 7) with 20 c.c. of red-fuming nitric acid and digest until the sulphur disappears. Dilute the acid with one and one-half parts of water, filter out any insoluble matter on a small paper, wash, add 5 drops of sulphuric, and evaporate the solution to dryness on the steam bath. Now dissolve the salts in 5 c.c. of cold water with the addition of 10 drops of hydrochloric acid and .1 gram of tartaric acid. Unless the arsenic is known to exceed .05 gram, filter

through a 2.5 cm. paper into a 25 c.c. beaker. Wash with a few drops of water from a fine jet and make slightly alkaline with strong ammonia (d., .90). The liquid should remain clear; if not, make the solution faintly acid and add another portion of tartaric acid.

Precipitation. — To the alkaline solution (volume 10 to 11 c.c.) add 3 c.c. of magnesia mixture (solution 23, Chapter III), dilute to 20 c.c. with the strong ammonia, and stir rapidly for five minutes. If the arsenic is excessive, use a 50 c.c. beaker for precipitation, increase the amount of magnesia mixture to 5 to 10 c.c., and add ammonia water equal to one-third of the volume of the solution.

Allow to stand overnight in a cool place, filter on a 2.5 cm. or 3 cm. washed filter, transferring the precipitate to the paper by pouring a little of the filtrate back into the first beaker. Wash with a fine jet of dilute (1 : 3) ammonia until the washings test nearly free from chloride when acidified and treated with a drop of silver nitrate. Dry the filter and contents in an oven at 100° to 105° C., remove the salt as completely as possible to a glazed paper, and place the filter in a weighed porcelain crucible. Add a few drops of a saturated solution of acid ammonium nitrate, char the paper very carefully, and repeat the treatment at low heat until the paper is consumed without a perceptible odor of arsenic. Transfer the remainder of the salt with the aid of a camel's-hair pencil and ignite very slowly until the ammonia is driven off, then at a full red heat over the Bunsen burner until two successive weights closely agree.

9. Determination of the Antimony, —in Absence of Tin. — The acid liquid remaining in the flask after distillation of arsenic, or the filtrate from the gravimetric separation of arsenious sulphide, contains all the antimony (and tin). The liquid remaining in the flask from a distillation process may also contain selenium, tellurium, bismuth, and a little copper. In such a case, dilute the hydrochloric acid solution until it contains one part of strong hydrochloric acid (d., 1.2) to five of water, and pass hydrogen sulphide to precipitate the metals. Extract the soluble sulphides as in methods 6, 7, for arsenic, using 15 c.c. of a colorless 15 per cent solution of sodium sulphide. If bismuth is present add a little potassium hydroxide, or treat the washed sulphide with hot, dilute potassium hydroxide alone (Smoot). Warm the solu-

tion and allow to stand for an hour or more, dilute, filter off the sulphide of copper, and wash the paper with dilute sodium sulphide.

Acidify the filtrate with dilute hydrochloric or sulphuric acid, and pass hydrogen sulphide into the liquid long enough to ensure an excess. Unless absolutely sure of its purity, it is well to extract this antimony sulphide again with colorless sodium sulphide to make sure that no copper remains. Then acidify the filtrate with dilute acid and saturate with hydrogen sulphide as before. The antimony sulphide contains more or less sulphur. It is best to filter it on a small paper, transfer the paper and contents to a small beaker, and add enough fuming nitric acid to make the solution colorless when the paper is destroyed. Bassett and Merrill recommend the following: Add 2 c.c. of (1:1) sulphuric acid and evaporate just to fumes of sulphur trioxide; dilute, add 1 or 2 c.c. of hydrochloric acid, filter to remove possible silica, etc., and saturate again with hydrogen sulphide. This precipitates clean antimony sulphide. Filter on a weighed Gooch crucible made up with a paper disc and asbestos, extract with carbon bisulphide, wash with alcohol and ether, and dry in an oven at 100° C. According to A. M. Smoot, the last two precipitations may be avoided by collecting the antimony sulphide (if free from copper) on a small weighed asbestos pad. Wash with water containing hydrogen sulphide, and suck the pad quite dry. Add a single drop of strong nitric acid which should not saturate the pad. Warm the crucible gently until the acid is expelled and then add one drop of fuming nitric acid. Do this very carefully to avoid saturation and yet reach all the sulphide. Warm gently to expel the acid, ignite the antimony to oxide (Sb_2O_3), and weigh. The electrolytic methods, noted at the beginning of this chapter, are not suitable for copper containing only a trace of antimony.

10. Separation of Antimony from Tin.—Distilled water and acids sometimes contain traces of tin. If the antimonious and stannous acids, resulting from the oxidation of the pure sulphides, are evaporated to dryness with five drops of sulphuric acid, the residue may be directly treated by the method of G. W. Thompson. The antimony is precipitated, alone, by hydrogen sulphide from a special solution, and the filtrate electrolyzed.

Dissolve 5 grams of pure oxalic acid and 5 grams of crystallized ammonium oxalate in 100 c.c. of water, pour the mix-

ture on the residue to be tested, and boil for half an hour, if necessary, to dissolve the salts. If sodium sulphide was used in the first extraction of the soluble sulphides, a little silica will remain insoluble. Filter this out, and wash the paper twice. Treat the silica in a platinum dish with a very little hydrofluoric acid and evaporate to dryness with a little hydrochloric acid. If any residue appears, boil it with a little acid-ammonium oxalate mixture and add it to the principal solution of the antimony. Heat the oxalate solution to boiling, pass hydrogen sulphide for fifteen minutes, filter off the antimony sulphide, and wash with hydrogen sulphide water. Saturate the hot filtrate again with hydrogen sulphide and filter. If considerable tin is present, a trace may be held in the paper. To remove it, dissolve the sulphide of antimony in a very little ammonium sulphide, pour the solution gradually into a fresh boiling solution of the mixture of oxalic acid and oxalate, and saturate again with hydrogen sulphide. One separation is usually sufficient to separate a trace of tin. The presence of traces of tin may be due to the use of water, delivered from tin-lined condensers.

The antimony is then treated as directed in the preceding method 9.

Tin. — The tin may now be recovered from the acid oxalate solution by direct electrolysis. This gives better results with small amounts of tin than the deposition in sulphide solutions. Boil out the hydrogen sulphide, cool the solution, and electrolyze with a current of .8 ampere per square decimeter of immersed cathode surface. The anode should be rotated 500 times per minute, or the electrolyte may be stirred by a stream of air which is caused to bubble up under an inverted funnel; a device recommended by J. G. Fairchild. The deposition of a large amount of tin may be completed in two and one-half hours. The end-point is indicated by a cessation of the gas evolution and by a slight alkalinity of the solution to litmus paper. Wash the deposit with water, alcohol, and ether. Dry gently over a lamp, or in an oven, and weigh. Dissolve the deposit in dilute nitric acid and correct the weight of the tin for any iron which may be found in the filtrate.

Detection of Traces of Tin. — To obtain a positive indication of a minute amount of this element, the older gravimetric method may be employed. Evaporate the oxalate solution to

fumes with an excess of sulphuric acid, following the removal of the antimony. Dilute the acid solution and precipitate the tin as stannous sulphide. Filter, wash, ignite slowly in a weighed porcelain crucible, and weigh as stannic oxide. Test the precipitate for copper and iron by fusion with a pinch of sulphur and sodium carbonate and extraction with water.

For the direct determination of tin in copper, without regard to other elements, consult "special methods for tin," 16, Chapter XIII.

CHAPTER XIII

SPECIAL METHODS FOR FOREIGN METALS IN COPPER

BISMUTH

1. Determination as Oxychloride. — One description will be sufficient for the similar modifications devised by A. M. Smoot and H. Koch. The principle involved is the precipitation of the bismuth as oxychloride, BiOCl , from a neutral solution. (An electrolytic method for bismuth with lead is given as method 9.)

For the detection and estimation of the minute quantities of bismuth present in refined copper, dissolve 50 to 100 grams of the drillings in 175 to 350 c.c. of strong nitric acid, diluted with 100 c.c. of water; boil the liquid and add a little more hydrochloric acid than the amount required to unite with the silver. Dilute the solution to 500 to 700 c.c. and add ammonium hydroxide by degrees until a small precipitate of copper hydroxide remains undissolved after stirring. Allow to settle in a warm place overnight, filter, and dissolve the precipitate in hot 15 per cent nitric acid. Any silver chloride will remain insoluble. If much is present, wash it from the paper into a small beaker and boil it for a few minutes in a beaker with the 15 per cent nitric acid.

Filter through the original paper and wash with hot dilute nitric acid. The liquid should be quite clear except when considerable antimony is present. If the liquid is clear, evaporate it to dryness on the steam bath, add 3 or 4 drops of hydrochloric acid and 5 c.c. of water, or more if required, to make a perfectly clear solution. With care, a solution measuring less than 10 c.c. and containing only 2 or 3 drops of hydrochloric acid may be obtained. Dilute this slowly with water to 150 c.c., thus precipitating the bismuth slowly as BiOCl . Since the oxychloride may be contaminated with a little copper, redissolve and precipitate again as above.

If antimony is present, the first precipitate obtained by ammonia must be dissolved in dilute hydrochloric acid and the

metals thrown down as sulphides. Filter, and boil the filter and contents with dilute potassium hydroxide and sodium sulphide to dissolve any antimony or arsenic. Wash the insoluble sulphides with water containing a little of the same reagent, dissolve them in nitric acid, and proceed as before. Filter the purified oxychloride of bismuth on a small asbestos pad, which has been thoroughly extracted with acid, dried, and weighed before use. Dry the filter and deposit in the Gooch crucible at 100° to 105° C. and weigh. Dissolve the bismuth compound in hot 25 per cent hydrochloric acid, wash the pad with water, taking care that no fine hairs become detached in the operations; then dry and weigh again, taking the weight of the oxychloride by difference.

2. Colorimetric Method (a). — The original process of F. B. Stone¹ has been somewhat modified. Dissolve 50 grams of metal in 200 c.c. of nitric acid, heat to expel red fumes, and dilute to 1000 c.c. Add a small crystal of ferric sulphate, or ferric alum, and make ammoniacal, continuing the addition with stirring until the copper hydroxide redissolves. Add also .75 gram of pure ammonium carbonate and 5 c.c. of sodium phosphate solution. Heat to boiling and allow to settle for several hours in a warm place.

Filter off the precipitate, wash with a little dilute ammonia, and dissolve the precipitate in a little hot dilute sulphuric acid, preserving the filter which might contain a trace of basic chloride. Dilute the solution and pass hydrogen sulphide for thirty minutes. Filter on the original filter and wash with hydrogen sulphide water. Add 10 c.c. of a saturated solution of yellow ammonium sulphide and warm until the sulphides are dark and the supernatant liquid clear. (Potassium hydroxide with a little sodium sulphide may be used, as bismuth sulphide is slightly soluble in the sodium compound, alone.)

Filter, and wash with the alkaline reagent, much diluted. Then dissolve the insoluble residue by boiling with dilute 15 per cent nitric acid, and separate it from the paper. According to F. B. Stone, the last traces of copper may be removed by repeated precipitation with ammonia and ammonium carbonate. This gives results which are a little too low. It is better to make slightly alkaline, then add a little pure potassium

¹ *Amer. J. Anal. Chem.* **1**, 411.

cyanide in sufficient amount to dissolve the copper sulphide. Then precipitate the bismuth with a trace of lead by hydrogen sulphide.

Filter on a small paper, wash thoroughly with hydrogen sulphide water, and redissolve in a little hot 15 per cent nitric acid. Evaporate to fumes with .5 c.c. of sulphuric acid, dilute with 5 c.c. of water, and filter into a test tube, or colorimeter. Wash the filter with no more than 5 c.c. of dilute sulphuric acid, thereby preventing the solution of any lead sulphate. Add a few drops of a 10 per cent solution of pure potassium iodide, and, afterwards, a few drops of strong sulphurous acid to remove any trace of iodine set free by a trace of ferric sulphate.

Finally, compare the tint of the liquid, after diluting to a known mark, with measured portions of a standard solution, which have been similarly treated with potassium iodide and sulphurous acid. One c.c. of the standard contains .0001 gram of bismuth.

Second Option (b). — The copper may be removed from the sulphate solution by alkaline thiocyanate, according to general method 1, Chapter XII. When this method has been used, an aliquot part of the solution is clarified by filtration, the excess of thiocyanate and sulphur dioxide removed by heating and adding a little nitric acid, and the bismuth precipitated by hydrogen sulphide. It is then purified from traces of copper and lead sulphides by the operations already described.

IRON AND MANGANESE IN METALLIC COPPER

3. Separation from Copper by Electrolysis. — Methods 1 to 5 of the chapter immediately preceding describe the treatment of solutions of copper containing considerable arsenic, etc., up to the point where the arsenic and associated elements, with the last traces of copper, have been precipitated by hydrogen sulphide. The filtrate is then freed from hydrogen sulphide and most of the sulphuric acid by evaporation, the residue dissolved, and the iron and associated metals determined as recommended in the following paragraph.

Dissolve 50 grams of clean drillings, strictly free from dust, etc., in a 750 c.c. beaker by means of the 320 c.c. of the "standard acid mixture" adapted for the electrolytic assay (Chapter XI). The acid should be added in two portions. If no definite

acid mixture is on hand, treat the copper with 250 c.c. of distilled water, 80 c.c. of pure sulphuric acid (d., 1.84), and two portions of 25 to 28 c.c. of nitric acid.

Care should be taken that the first acid is free from a trace of manganese. C. P. sulphuric acid often shows this impurity. A careful blank analysis of all the reagents and distilled water should be carried along with each set of copper samples.

The solution may be diluted to 700 c.c. and electrolyzed in the large Frary solenoid, described in Chapter I, or the ordinary cathode may be combined with a rotating anode of platinum. If necessary, the solution may be washed into a 500 c.c. beaker and diluted only to 450 c.c., provided that the current is started immediately in the solenoid to prevent crystallization. The current used is 5 to 7 amperes and the time required, seven to fourteen hours. The cathode may be a coarsely perforated platinum cylinder, 11 cm. in height and 7 cm. in diameter, made by bending and riveting a single sheet. A narrow double seam may be formed inside, into the fold of which a wire stem is inserted but not riveted. As soon as the liquid becomes colorless, wash down the glass covers. In half an hour, withdraw the electrodes, and wash them with water, allowing the washings to drop into the electrolyte. Evaporate this solution rapidly on the hot plate, protecting it from dust by a suspended cover. Transfer the thick sirupy liquid to a 3a porcelain casserole and heat strongly until all the free acids and most of the acid ammonium sulphate are expelled. Dissolve the residue in 10 drops of hydrochloric acid and 50 c.c. of water, then saturate the solution with hydrogen sulphide. Filter, wash the sulphides with water containing hydrogen sulphide, heat to boiling, and recharge. Reject the precipitated sulphides, unless antimony is to be determined according to methods 2 to 5, Chapter XII.

Iron and Manganese.—Concentrate the filtrate to 30 c.c., add a few cubic centimeters of bromine water to complete the oxidation, then boil out all the bromine and precipitate the ferric hydroxide with a slight excess of ammonia. Filter, redissolve in a little acid and water, and repeat the precipitation. Filter on an ashless filter, wash free from salts, and preserve both filtrates and washings. Some of the best sulphuric acid contains a trace of manganese which interferes with the nickel determination, and should be removed with the ferric hydroxide

by adding bromine and slight excess of ammonia and heating. Remove the traces of manganese from the ferric hydroxide by dissolving and precipitating with ammonia alone in presence of some ammonium chloride; very pure ammonia, free from iron and pyridine, should be used for this work.

COBALT, NICKEL, AND ZINC

Order of Determination.—The elements may be separated by a combination of accurate European methods, similar to that published by R. L. Hallett.¹ When the copper contains traces of cobalt with much nickel, it is best to separate the cobalt first by the process of Knorre and Illinski, making use of nitroso- β -naphthol (4). The determination is made in the filtrate from the ferric hydroxide. The filtrate from the cobalt is evaporated to fumes with sulphuric acid, cooled, diluted to 30 to 50 c.c., and the nickel separated by dimethyl glyoxime (method 5). In the filtrate from the nickel, the organic reagent is destroyed by evaporation to fumes with a slight excess of sulphuric acid. The zinc is then precipitated.

If the amount of cobalt is large compared with the nickel, reverse the order of separation. In most of the brands of copper the nickel is largely in excess, however. If nickel and cobalt may be reported together, the zinc may first be removed by hydrogen sulphide (method 6), filtered off, and the cobalt and nickel estimated together by electrolysis.

4. Cobalt.—The original procedure of Knorre and Illinski has been modified. To separate the cobalt from the nickel and zinc, acidify the filtrate from the iron precipitation in the first method with hydrochloric acid. Evaporate to 30 c.c. if very little cobalt is present, then add 4 c.c. of hydrochloric acid in excess. Warm, and add a hot saturated solution of nitroso- β -naphthol in 50 per cent acetic acid, until no more of the cobalt compound $[(C_{10}H_6O - NO)_3Co]$ is formed. After a few hours, filter, wash first with cold then with warm 12 per cent hydrochloric acid until the nickel salt is removed, then with hot water to remove all the acid. Reduce carefully in a Rose crucible with oxalic acid in a current of hydrogen; or ignite in a platinum crucible to oxide of cobalt, Co_3O_4 (factor .7344). A third method is more accurate than either form of

¹ *Eng. and Min. Jour.* **96**, 857 (1913).

ignition. Dissolve the red salt in dilute nitric acid, evaporate to fumes with 1 to 5 c.c. of sulphuric acid, dilute to 30 c.c., make strongly alkaline with ammonia, and electrolyze according to the conditions specified in 7.

5. Nickel.—The delicate reaction with dimethyl glyoxime, discovered by Brunck and Tschugaeff,¹ has been adapted to the analysis of copper. If the nickel is to be determined in the filtrate from cobalt, treat the filtrate from the separation in method 4 with 3 c.c. of sulphuric acid, evaporate to fumes, and dilute to 30 c.c.

If nickel is to be separated first, the filtrate from the iron precipitation is taken, and similarly treated.

Add to the clear acid liquid a 1 per cent alcoholic solution of dimethyl glyoxime in amount equal to nearly five times the nickel, and make the solution faintly alkaline with ammonia. Solutions from high-grade metal may be rendered alkaline at once and any trace of iron filtered out before the special reagent is introduced. Allow to stand on the steam plate until flocculent, then filter while hot through a weighed asbestos felt if a direct weight of the salt is preferred. Wash with hot water containing a few drops of ammonia, and dry at 110 to 120° C. to a constant weight. The compound ($C_8H_{14}N_4O_4Ni$) contains 20.325 per cent of nickel, Ni.

Traces of nickel may be weighed more accurately by dissolving the red salt in hot (1:1) hydrochloric acid without previous drying. Then add 3 to 5 c.c. of sulphuric acid and evaporate to strong fumes of sulphur trioxide, dilute to 30 to 100 c.c. (according to the amount of nickel present), and add 30 per cent by volume of ammonia (d., .90). Electrolyze as in method 7. It may prove beneficial with high nickel to add 15 c.c. of a saturated solution of ammonium carbonate to the electrolyte.

If more than a trace of zinc or cobalt is present, as in alloys, or scrap metal, it may be necessary to redissolve the nickel oxime in a little hot hydrochloric acid and reprecipitate. To recover the oxime itself for further use, make the weighed compound into a paste with a little water, warm it with potassium cyanide, filter hot, and precipitate at once with acetic acid. Wash and dry the substance. For the assay of nickel in crude material, refer to Chapter VII.

¹ *Zeitsch. Angew. Chem.* **20**, 834 and 3844.

6. Zinc, — With Separation of Cobalt and Nickel. — Two or three brands of commercial copper contain nickel as an important constituent. In such a case, the organic precipitates obtained by methods **2** and **3** are too voluminous for convenient manipulation. In the assay of such metal, it is better to remove the zinc first by hydrogen sulphide. The gas is expelled from the filtrate and the nickel and cobalt deposited on platinum. In routine work, a trace of zinc would be deposited and weighed with the other two elements. This determination is made on the filtrate from the iron precipitation of method **3**.

When a separation of cobalt and nickel has already been made by methods **4** and **5**, evaporate the last filtrate to fumes with 3 c.c. of sulphuric acid to destroy the organic matter, and dilute to 25 c.c. Make slightly alkaline with ammonia, then faintly acid with acetic acid or formic acid, and precipitate zinc by hydrogen sulphide.

In order to separate zinc from cobalt and nickel in solution, acidify the filtrate from the iron precipitation (method **3**) with either formic or glacial acetic acid, then add an excess of that acid equal to one-sixth of the volume of the cold solution. Saturate the cold liquid with hydrogen sulphide. Allow to settle, filter, test again with the gas current, and filter. Wash the filters with hydrogen sulphide water containing a little ammonium acetate, and if the sulphide is not white, redissolve and purify it from a trace of copper or lead. Ignite the purified sulphide of zinc and weigh it as oxide, containing 80.34 per cent of zinc. "Jena glass should not be used in copper analysis as it contains soluble zinc" (Smoot).

7. Cobalt and Nickel by Electrolysis. — In the filtrate from the zinc precipitation, boil out every trace of hydrogen sulphide. Make the solution ammoniacal and add an excess of ammonia (d., .90) equal to 30 to 40 per cent of the volume of the solution, which should have a final volume of 100 to 150 c.c. for .2 gram of cobalt or nickel. Better results are obtained if the acetic or formic acid in the filtrate from zinc is destroyed before electrolysis by evaporation to fumes with 5 c.c. of sulphuric acid. Cobalt and nickel are deposited on the usual type of split platinum cylinders in ten to fourteen hours with a current of .2 to .5 ampere at a potential of 2.5 to 2.8 volts. The test for the end-point is made by treating 1 c.c. of the electrolyte

on a porcelain spot plate with hydrogen sulphide water or alkaline sulphide. Wash the cathode finally with water and denatured 90 to 94 per cent alcohol, then ignite the remainder of the alcohol carefully in a flame, keeping the plate in rapid motion.

The revolving anode, or the Frary solenoid, permits the deposition to be completed in sixty to ninety minutes with a current of 3 to 4 amperes per square decimeter of immersed cathode surface and a potential of 5 volts. When cobalt or nickel is separated from the filtrates in methods 4 or 5, a trace of iron may be expected from impurity in the organic reagents. In spite of the ordinary care in separations, a trace of copper may also be present in the deposited metals.

NOTE. — Smith and Lukens have proposed to deposit cobalt as dioxide upon a platinized platinum anode from the double fluoride of cobalt and ammonium with a little nitric acid. The separation is said to be particularly accurate for traces of the metal. The anode deposit is ignited to Co_3O_4 .¹

LEAD IN REFINED COPPER

8. Author's Method.² — Dissolve 20 grams of wire-bar or casting copper, as drillings, in 100 c.c. of the purest nitric acid (d., 1.42), evaporate until a pellicle forms, and dilute to 500 c.c. with distilled water. If lower grade metal, containing more than .01 per cent sulphur, is to be tested, weigh out only 10 grams and treat with 60 c.c. of nitric and 15 c.c. of hydrochloric acid. Digest with fuming nitric acid and a little potassium chlorate if any sulphur remains undissolved. Evaporate to a sirup, add 40 c.c. of nitric, and evaporate again until a skin begins to form. Just before concentration, drop into the beaker .1 to .5 gram of pure sodium carbonate, or sufficient to unite with the sulphur present. Finally, neutralize the liquid with ammonia until a layer of copper hydroxide, about 3 mm. in thickness forms on the bottom. Place the beaker in a large-size Frary solenoid and electrolyze with a perforated cathode measuring 10 cm. in diameter and about 11 cm. in height. The anode may be a small, closed, perforated cylinder about 5 cm.

¹ *Trans. Am. Electrochem. Soc.* **27** (1915), 30.

² *J. Am. Chem. Soc.* **17**, 814.

high and 2 cm. in diameter, provided with a stem of heavy wire, 15 cm. in length. Cover the beaker with split glasses.

Electrolysis for Lead.— Provide a slow circulation of water in the narrow annular space between the beaker and the copper cylinder which forms the reel for the insulated wire (see Chapter I). Commence the electrolysis with a current of .5 ampere (ammeter reading), and after thirty minutes raise the current to 6 amperes for three and one-half hours additional. At the end of the second period, the lead in any refined copper will be entirely deposited. In the case of casting copper of uncertain purity, run for a third period of one hour with a second clean anode cylinder in order to obtain the last trace of lead as dioxide. Remove the anode very quickly, without complete interruption of the current; plunge it into a little beaker of distilled water, and then wash it carefully with a jet of water. Complete the washing with denatured alcohol followed by ether, and finally dry the lead deposit in a hot-air oven for fifteen minutes at 200 to 230° C.

After weighing the lead dioxide on the anode, either dissolve it in nitric acid containing a little hydrogen peroxide or a few crystals of oxalic acid, or immerse it in cold dilute nitric acid in contact with a strip of copper. The deposit will dissolve in a few minutes. Dry and weigh the plate again. It is incorrect to weigh the anode before electrolysis as it always loses a little weight during the operation.

For Lead with Bismuth.— A trace of bismuth oxide, if present in solution, may deposit with the dioxide of lead. In such a case, dissolve the peroxide with 5 to 10 c.c. of a mixture of strong nitric and oxalic acids, add a few drops of sulphuric acid, and evaporate to fumes. Dissolve in 5 c.c. of water, filter on a very small filter, wash with a few drops of dilute sulphuric acid, and test the filtrate for bismuth by method 2 of this chapter.

A careful test should always be made for a trace of lead in the nitric acid. In order to secure the same conditions, evaporate the requisite amount of nitric acid almost to dryness. Add the remaining acid, about 10 c.c., to a solution of 20 grams of a high-grade copper, from which every trace of lead has already been removed by repeated electrolysis. Insert electrodes and pass the current as in the regular analyses. Any traces of

manganese will remain in solution. Treat the weighed anode with the reagent to dissolve any lead, then wash, dry at 200°C ., and weigh again. Deduct the amount of lead oxide obtained in the "blank" from the result of the analysis. The factor required to reduce lead dioxide to metallic lead, when treated as described, has been determined by E. F. Smith and others to be .8643.

9. Lead — First Modification. — As a check method for minute traces of lead, A. M. Smoot recommends the solution of 50 grams of the borings in 200 c.c. of nitric acid (d., 1.42). Dilute the solution to 700 c.c. and electrolyze long enough to remove the lead, employing a Frary solenoid, or large anode and rotating cathode. Remove the anode without interrupting all the current, and wash and dry as in the first modification of the electrolytic method. Dissolve the weighed dioxide of lead in dilute nitric acid with the addition of a few drops of hydrogen peroxide in a small beaker. Add 3 c.c. of sulphuric acid and evaporate to fumes. Cool, dilute to 20 to 25 c.c. with water, boil, and allow to stand overnight, if the lead is to be weighed as sulphate.

The sulphate may be filtered off, dissolved in alkaline tartrate, and electrolyzed by Dr. Toisten's formula (10), but the author considers it more accurate to determine the traces of oxides of manganese, tin, or bismuth which may be present in the weighed deposit of lead dioxide, and deduct the observed correction. In the determination of lead in bronze, or other copper carrying considerable tin, a trace of stannic oxide may be expected in the lead. When the amount of lead is known to be considerable, it is advisable to interrupt the current twice for a moment or two, in order to favor the resolution of any trace of lead which may have been carried over on the cathode.

10. Deposition as Metallic Lead. — Dr. Toisten separates small amounts of bismuth from lead, or copper, by the electrolysis of a hot glucose, or sodium tartrate solution, acidified with 2 c.c. of nitric acid. The author fails to obtain any good separation, but a third solution recommended for the deposition of considerable amounts of lead as metal furnishes very good results. Lead nitrate, dioxide, or sulphate (after separation from copper by previous methods), is dissolved in a solution containing 1 c.c. of nitric acid, 20 grams of tartaric acid, and 20 c.c. of concentrated ammonia. Dilute to 110 c.c. and electrolyze at a boiling heat

with a current of 2 amperes at 1.4 volts potential. With an anode revolving 800 to 1000 turns per minute, the deposition will be completed in ten minutes if the lead weighs less than .3 gram. The deposit on the cathode is washed, dried at 100° C. or less, and weighed.

SULPHUR

11. Author's Method for Refined Copper.—After the lead has been removed from the electrolyte as dioxide (according to 8 or 9), insert a clean anode wire or cylinder in the beaker of copper solution, prepared from a 20-gram sample of drillings. Cover the beaker, and continue the electrolysis with a current of 6 amperes, or 4 amperes overnight. As soon as the liquid is perfectly colorless, remove and wash the electrodes into the solution. Concentrate the liquid upon a plate over a flame which has been proved to be free from sulphur compounds. Great care must be taken to prevent exposure of the solutions during the analysis to fumes of hydrogen sulphide, or sulphuric acid. In fact the operations should be conducted in a special room, if possible. All containers should be rinsed with nitric acid and distilled water before use.

As the solution concentrates, transfer it gradually to a 7 or 9 cm. casserole, and remove the residual ammonium nitrate by careful evaporation to dryness in the covered dish with an excess of hydrochloric acid. Dissolve the salt in a very little water and evaporate again on the steam plate with excess of hydrochloric acid. Repeat the operation. If a trace of copper was observed in the first residue from evaporation, remove it entirely before the hydrochloric acid is added, by electrolysis in small volume with a narrow platinum strip. Filter the pure hydrochloric acid solution into a 50 c.c. lipped beaker. Then heat the clear liquid to boiling, add 3 to 5 c.c. of a saturated solution of barium chloride, and allow to stand overnight. The solution should contain only a few drops of acid. Copper, if present in more than traces, retards or prevents the precipitation of traces of barium sulphate. The precipitation may be completed in 3 hours at 75° C. Filter on a 5 cm. close, washed paper and ignite in a small weighed porcelain crucible. Barium sulphate (BaSO_4) $\times 0.1373 = \text{Sulphur (S)}$.

Modification for Converter, or Blister Copper.—Dissolve a 5-gram sample in a sufficient amount of nitric acid mixed with

hydrochloric to oxidize the sulphur without the formation of globules. Evaporate the solution repeatedly with nitric acid until the hydrochloric acid is removed. Filter off any insoluble matter, wash, and boil the residue with a few cubic centimeters of a saturated solution of sodium carbonate, in order to convert any trace of lead sulphate to carbonate and form a soluble sulphate. Filter off any insoluble matter, wash once, and evaporate to dryness with an excess of hydrochloric acid. Dilute until the residue dissolves and test for a trace of sulphates by barium chloride.

Electrolyze the copper solution and conduct the remainder of the test as directed in the method for refined copper. A little potassium chlorate or bromine will also be required to oxidize all the sulphur in crude metal.

DEOXIDIZING ELEMENTS

12. Aluminum, Boron, Manganese, or Phosphorus. — These seldom occur in any commercial copper unless added in some special crucible treatment in the foundry. The determination of these elements in quantity is described in the next chapter. Small amounts of these elements, which have been added as deoxidizers, may be detected as follows:

Electrolyze a nitric acid solution of the copper drillings in the same manner as for the lead determination. Test the anode deposit for manganese, or simply dissolve any slight deposit and return it to the solution. Evaporate the solution to dryness to test for manganese. A complete deposition of traces of manganese on an anode can only be obtained from a sulphate solution of small volume. To obtain *phosphorus* from the electrolyte, concentrate to a small volume and precipitate by ammonium molybdate from the hot solution, according to methods of iron analysis.

Lucien Robn states that minute traces of *boron* may be detected in solution by the addition of tincture of mimosa blossoms.¹ Determine according to Fresenius.² *Aluminum* will be precipitated as hydroxide with the iron (in the determination of iron), and may be separated therefrom by the methods adopted for alumina in slags, Chapter V.

¹ *Proc. 8th Inter. Congress of Appl. Chem.* **1**, 429.

² *Quant. Anal.*

OXYGEN AND OCCLUDED GASES

13. By Ignition in Carbon Monoxide.—Mr. T. West has proposed to heat copper, or brass, in but one gas, carbon monoxide, CO. A high heat must be maintained to obtain any quantitative reduction, and as yet the writer has not succeeded very well with this operation. The temperature recommended is 900° C. for copper and up to 1050° for brass, the time varying between two and three hours. It is claimed that, in spite of the volatility of zinc, the oxides may now be determined in brass. The zinc is condensed in special apparatus and the carbon dioxide is absorbed and weighed. The carbon monoxide may be generated by the method given in Chapter III, and must be purified from carbon dioxide and oxygen.

14. Author's Method,—Ignition in Hydrogen and Carbon Dioxide.—Dr. Hampe¹ first proposed that oxides in copper should be accurately determined by the loss of weight sustained by finely divided copper when reduced in pure hydrogen, or by the weight of water produced. The author has proved that additional precautions must be taken to correct for certain errors inherent in the original method.

First:—Traces of sulphur are evolved, and when accurate results are desired, the hydrogen sulphide should be absorbed in ammoniacal cadmium chloride, and the trace of sulphur determined by titration with iodine, and deducted from the *apparent* loss of the copper.

Second:—The apparent loss of the copper when heated in hydrogen to constant weight, includes a trace of occluded gases, and occasionally moisture, present in the original metal. These may be expelled by a preliminary heating in carbon dioxide, although the quantity is so small as to be negligible in ordinary work. The water formed may be weighed and one-ninth of the weight taken as "occluded gas," because the gas is principally hydrogen.

Third:—About .01 per cent of hydrogen by weight is retained by the copper after reduction in a current of hydrogen at a red heat. This error has already been noted and corrected in the author's modification.² Since copper has practically no affinity for carbon dioxide, a subsequent heating for twenty

¹ *Z. für Berg Hütten und Salinen Wesen*, 1873.

² *J. Ind. and Eng. Chem.*, 4 (1912), 402.

minutes in the latter gas will expel the remaining hydrogen. The carbon dioxide is finally expelled by dry air after cooling. "Over-poled" copper contains more gas than metal of lower pitch.

METHOD

Preparation of the Copper for Ignition. — In exceptional cases, it may be necessary to dry a sample of *porous* metal at 100° C. in an atmosphere of pure nitrogen, or carbon dioxide. Any oil may be removed from drillings by ether. Samples should be taken with a clean drill, and the speed and diameter regulated to produce small chips, free from any trace of oxidation by heating. A fair sample may be obtained from a casting by observance of the "copper specifications" of the American Society for Testing Materials. In order, however, to measure the exact relation between the copper and oxygen in a sample, it is necessary to determine the oxygen on the same bottle of fresh drillings that is used for the estimation of copper and silver by electrolysis. The oxygen varies inversely as the copper content of a casting, and although .005 to .01 per cent may be a good check in electrolysis, it constitutes a large percentage error in an oxygen determination.

A. M. Smoot notes that it is almost impossible to remove all the soapy lubricant from some drawn wires by direct washing with alcohol or ether. Such material may be cut in short pieces and digested for a few minutes with a 1 per cent solution of potassium hydroxide in alcohol, having the liquid warm but not hot enough to oxidize the metal. Finally, wash with water, alcohol, and ether, in rapid succession. If a slight abrasion of the "skin" of the wire is not objectionable, the wire may be scoured with wet sharp silica, which has been ground to pass through a sieve of 40 meshes to the linear inch. The wire may then be cut up, treated with alcohol and ether, and dried off at a low heat.

Preparation of Pure Carbon Dioxide. — A pure gas for research may be prepared by the method of Bradley and Hale,¹ who generate the gas by the action of strong sulphuric acid on a paste of sodium bicarbonate and water. This process requires too much apparatus and attention for technical analysis. Carbon dioxide of sufficient purity may be generated from pure

¹ *J. Am. Chem. Soc.* **30**, 1090.

white lump marble, or calcite, provided that proper reagents are used to absorb the traces of oxygen and hydrocarbons which are continuously evolved. A trace of oxygen in the carbon dioxide or hydrogen will produce a dark tint on the hot reduced metal at the point where the gas enters the bulb.

The purification train of tubes is arranged in order as follows: (a) Casamajor or small Kipp generator with an elevated pressure bottle. The apparatus should be small enough to permit the expulsion of every trace of air in thirty minutes' evolution before the gas is passed over the copper. (b) Bulb containing a saturated solution of mercuric chloride for the absorption of hydrocarbons. (c) A glass tube containing a saturated solution of silver sulphate in dilute sulphuric acid. (d) A Bowen's potash bulb with strong sulphuric acid. (e) A preheating tube for removal of traces of oxygen. This consists of a 25 cm. ignition tube in which is tightly fitted a 15 cm. roll of copper gauze. The tube is heated to a low red heat by two fish-tail burners, but the gas should not be lighted until the air has been driven out of the bottle and tubes, to prevent rapid oxidation and deterioration of the copper. This gauze may be regenerated in fifteen minutes by reversing the valves and passing hydrogen from the companion generator. (f) Last in the gas train are two drying tubes filled with strong sulphuric acid or phosphoric anhydride as preferred. The phosphoric anhydride is opened up with glass wool. (g) The train from this generator and the one producing hydrogen are finally connected to each arm of a glass tee, provided with two three-way valves. The valve from the carbon dioxide bottle is arranged to discharge into the air for thirty minutes before the gas is used in order to remove the last traces of oxygen. After the three-way valve is placed a hard glass tube one foot in length, having one large bulb or two of smaller size. A silica tube with porcelain or alundum boats may also be used to hold the 50- or 100-gram sample of fine copper drillings.

Preparation of Pure Hydrogen. — This generator should also be of rather small size in order that the air may be quickly swept out. The gas may be more easily purified if it is generated from pure zinc and dilute sulphuric, instead of hydrochloric acid. In accordance with a suggestion of A. M. Smoot, one drop of a 10 per cent solution of platinic chloride is added to two

liters of (1 : 4) sulphuric acid. This trace of platinum promotes a steady flow of gas. Good hydrogen may, of course, be purchased, if preferred. The purifying train consists of: (a) The generator or gas cylinder; (b) Allihn washing bottle containing a 10 per cent solution of potassium hydroxide, saturated with potassium permanganate; (c) tubes for the removal of traces of oxygen, in which there is a choice of three alternatives, the first being preferred. The first is an Allihn 250 c.c. bottle of potassium hydroxide solution (d., 1.27) in which is dissolved 5 grams of pyrogallic acid; second, a heated tube of 5 per cent palladium asbestos; or third, a tube containing a long roll of reduced copper gauze or turnings, heated in a short furnace. (d) Two tubes of drying reagent follow. The same reagents

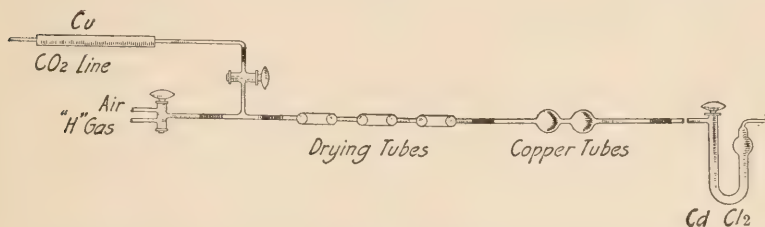


Fig. 16.—Section of Apparatus for Estimation of Oxygen in Copper.

should be placed before the copper to dry the gas that are placed after the ignition tube to catch any evolved moisture for weighing. Bulbs of strong sulphuric acid are efficient, or glass-stoppered tubes of phosphoric anhydride mixed with glass wool. The general custom has been to determine the oxygen by the loss in weight of the copper sample. The gas passing over the red-hot drillings is passed through a small U tube or bottle containing 10 c.c. of a 2 per cent solution of ammoniacal cadmium chloride in order to absorb traces of evolved sulphur. By a combination of tubes, the water may also be weighed.

Ignition. — The reduction may be made in a hard-glass tube about 30 cm. long and 6 mm. internal diameter, provided with one large, or two small central bulbs. The tube is placed on a lamp ring of 10 cm. diameter and is protected from over-heating by wrapping it with a piece of asbestos paper, clamped with a loop of stiff wire. The estimation of the oxygen by simple loss in weight, without corrections, is rapid but approximate. For

such a test, four samples of 20 grams each may be placed in weighed boats in a combustion tube heated by an ordinary gas furnace. The electric furnaces adopted for carbon in steel are efficient but heat very slowly.

Analysis. — Clean, ignite, and weigh the tube or boat to be used. Weigh about 50 grams of the fine clean drillings, or filings, and feed them into the central bulb of the tube by stopping one end with a glass rod, and using at the opposite end a short funnel, into which the drillings may be fed with the aid of a stiff wire. After the material has been packed by tapping, the tube should be wiped dry with a warm cloth, and allowed to stand on the balance for ten minutes before weighing. Connect the bulb tube to the gas apparatus and make sure that the joints are all tight. Pass pure carbon dioxide through the cold tube for thirty minutes, if occluded gases are to be investigated.

Occluded Gases. — If some knowledge of the gases is desired, heat the bulb tube to a red heat for twenty minutes in the current of carbon dioxide. The bulbs should be protected by wrapping with asbestos paper held in place with a stout wire. Three Bunsen burners give sufficient heat. The tube is then cooled by an air blast, the carbon dioxide finally being expelled by the passage of a current of dry air for ten minutes. Wipe the tube clean and allow to stand in the balance ten minutes before taking the final weight to determine the loss in ignition. One-ninth of the loss expresses approximately the original gas, as it is principally hydrogen, and would abstract oxygen from the copper to form water vapor. For the purposes of analysis, it is sufficiently accurate to omit this ignition in carbon dioxide, and ignite in hydrogen at once. (The tube used by Dr. H. O. Hofman will contain 100 grams of copper.)

Oxygen. — Connect the drying bulbs with the copper sample tube and attach a U tube containing 10 c.c. of the ammoniacal solution of cadmium chloride. Pass a current of pure hydrogen through the cold tube for fifteen minutes at the rate of one large bubble, or four small ones, per second, in order to expel all the air. Now raise the tube to a good red heat by a furnace or triple burner, and maintain the temperature below the point which would cause the metal to distil into the glass. Heat one hour if the sample is reduced to filings, or two hours for fine drillings. The necessary time should be determined by experi-

ment for drillings of the size to be tested. Twenty to thirty minutes before the reduction in hydrogen is completed, the carbon dioxide generator should be started, as already directed, and allowed to discharge into the air at the three-way valve. A quick turn of two glass valves will then substitute carbon dioxide for hydrogen, and twenty minutes additional heating in the carbon dioxide will expel the hydrogen (about .01 per cent) which would otherwise have been retained by the copper. Cool in the current of carbon dioxide for ten minutes, using a small air blast, and then replace the gas by dry air from a pipe attached temporarily to the three-way valve. Place in the balance and weigh in ten minutes.

To determine the correction for the traces of sulphur evolved, place 70 c.c. of water in a tall No. 1 beaker, and transfer the cadmium solution and sulphide as rapidly as possible with the aid of 30 c.c. of (1:1) hydrochloric acid. Titrate at once with standard iodine. If 2 grams of iodine are dissolved in one liter of water, 1 c.c. will equal .00025 gram of sulphur. Deduct the weight of sulphur from the apparent loss of weight of the copper, and the result will express the weight of oxygen in the metal.

A check, or experimental proof of the completeness of the reduction, may be obtained by a careful electrolytic assay of the reduced drillings from the tube, correcting the assay for the trace of copper in electrolyte.

Rapid Method.—In routine work, results may be obtained in quicker time by heating several samples in one tube in porcelain boats for two hours. If cooled in hydrogen (after Cobeldick), the method is more rapid, but approximate. If finally heated and cooled in carbon dioxide, as recommended by the author, the only appreciable error is that due to the loss of a trace of sulphur.

15. Photo-micrographic Method.—Following Heyn,¹ and the work of Hofman, Green & Yerxa² in the measurement of a microscopic field with a planimeter, E. S. Bardwell³ projects the area of the microscopic field directly upon a piece of duplex paper in a 16-inch circle, and then traces and cuts out the copper areas, leaving a net-work of paper, representing the eu-

¹ *Mittheil. aus den Königl. Versuchsanstalten zu Berlin* **18**, 315.

² *Trans. A. I. M. E.* **34**, 671.

³ *Ibid. Bull.* **79** (1913), 1429.

tectic. The two lots of paper are carefully weighed and the weights are proportional to the areas of copper and eutectic ($\text{Cu} + \text{Cu}_2\text{O}$ containing 3.45 per cent Cu_2O).

The polished copper is etched by heating it for three or four minutes in a current of hydrogen gas at about 300°C ., or low red heat, first passing the gas for ten minutes to drive out the air. This scheme can only be approximate in the case of cast copper because there is so much variation in the crystalline aggregates, and it requires about as much time per sample as the rapid method already described in 14.

TIN IN COPPER

16. Special Method. — The separation of tin from antimony or arsenic has been described (10, Chapter XII). Copper refined from foundry scrap, or from metal which may have been electrolyzed with lead anodes, will occasionally contain a trace of tin. The following is developed from the method of W. H. Bassett, devised for this material.

Dissolve *two* portions of 75 to 100 grams each in 500 c.c. of distilled water and 250 to 300 c.c. of pure, strong nitric acid. The distilled water employed should not be distilled from a tin-lined condenser. After the acid has been added gradually and the copper has dissolved, boil the solutions down to a sirup. When a skin begins to form on the surface, cool slightly, dilute with a few cubic centimeters of nitric acid and 600 c.c. of water, and heat until all is dissolved. If a little basic copper remains, add a very little acid until it clears up, and allow to stand on the steam plate for at least two hours but better overnight. The solution should not be allowed to cool until it is filtered. Pass both solutions through the same small doubled filter, reserving all insoluble residue until the last. Remove the large beaker and replace by a small clean beaker, then transfer the residue to the filter. The precipitate may contain a trace of iron and phosphate of tin, also a part of the antimony present. It may be purified by the method used in the analysis of bronze, Chapter XIV. Dissolve the tin oxide, etc., in a little yellow ammonium sulphide containing about 3 per cent of pure ammonium chloride. Filter, precipitate the tin with a slight excess of acetic acid, and filter again. Wash with water acidified with acetic acid, and ignite carefully to

oxide with the precautions noted in Fresenius' *Quantitative Analysis*.

SELENIUM AND TELLURIUM

17. Special Method. — The rapid combination method of the author for the estimation of the two elements, in connection with the arsenic and antimony, has already been described (7, Chapter XII), and is recommended. The papers of E. Keller¹ and C. Whitehead² present two original schemes which are slower, but are capable of equally good results. The elements are separated by excess of ferric hydroxide. The copper must be completely removed by repeated treatment, or a loss will result when the ferric hydroxide is finally dissolved in acid and the solution treated with hydrogen sulphide. If any silver, or copper, is present, some silver or copper selenide may be formed, which is afterwards insoluble in alkaline sulphides. Proceed as in the next paragraph.

Dissolve two portions of 50 grams of refined copper in separate beakers, using in each case 200 c.c. of nitric acid (d., 1.42), of tested purity. Add to each 30 c.c. of a 10 per cent solution of ferric ammonium sulphate, or 2 grams of ferric nitrate, render sufficiently ammoniacal to redissolve all the copper hydroxide formed, then heat to boiling and allow to settle. Filter, wash with dilute ammonia, wash most of the ferric hydroxide into the original beaker, and dissolve in (1:20) sulphuric acid with a little hydrochloric. Precipitate again and filter on the same filter. Repeat the operations until the filtrate shows no blue color of copper. Finally, dissolve the hydroxide in the least possible amount of hydrochloric acid diluted with 10 volumes of water. From this point, there are two or three separations which are a matter of individual preference.

(a) *Modification of E. Keller.* — Saturate the cold hydrochloric acid solution of the ferric hydroxide, etc., with hydrogen sulphide gas. Copper must be absent and the solution must be cold to render the selenium sulphide soluble in sodium sulphide. Filter, wash, and digest with a little sodium sulphide solution. Filter off insoluble matter, wash the filter, acidify the solution with nitric acid, and evaporate to dryness. The latter operation must be performed with care on the water bath or steam plate. If five drops of sulphuric acid are added during concentration, no

¹ *J. Am. Chem. Soc.* **22**, 242.

² *Ibid.* **17**, 280.

nitric acid will remain in the residue. To this residue add 180 c.c. of hydrochloric acid (d., 1.2) and 20 c.c. of water. Boil just long enough to destroy any nitrous compounds and reduce selenium and tellurium to the lower chlorides. If the salts are not excessive, 90 c.c. of acid with 10 c.c. of water are sufficient, and, if the sulphuric acid was added exactly to replace the nitric, it is better to heat just to boiling and then remove to prevent loss of selenium. Cool the solution and filter out any sulphur or insoluble halide through an asbestos felt on a Gooch crucible. Wash the residue several times with 90 per cent hydrochloric acid. The filtrate is now ready for saturation with sulphur dioxide gas, which may be supplied from a steel cylinder, or generated by copper borings and acid.

The author prepares the sulphur dioxide more easily from a solution of sodium sulphite which is allowed to drop into strong sulphuric acid (Chapter III). Charge the hot solution with the gas, allow to cool while charging, and set the beakers away until the precipitate has settled. Filter the selenium on a weighed Gooch felt and wash three times with 90 per cent hydrochloric acid. Set the filtrate aside and wash the selenium free from salts by successive treatment with dilute hydrochloric acid, water, and strong alcohol. Dry at 100 to 105° C. for one hour, cool, and weigh immediately. Saturate the solution with the sulphur dioxide a second time to be sure of complete precipitation.

The filtrate from the second precipitation contains the tellurium. Add water to double the volume, then boil the solution for several minutes, while sulphur dioxide is again conducted through the liquid. Filter when cooled, wash, dry, and weigh as before. The felts containing both selenium and tellurium may be ignited to drive off the two elements, and the felts reweighed as a check. With some asbestos, there is a notable difference between the ignited weight and the weight after moistening the ignited felt and drying in an oven at 105° C. The latter weight corresponds to the original dried weight of the felt.

(b) *Modification of C. Whitehead.* — The preceding method is exactly followed until the solution of ferric hydroxide has been obtained, strictly free from copper salts. Add 1 gram of solid tartaric acid, make alkaline with an excess of potassium hydroxide, and pass hydrogen sulphide gas into the solution for thirty

minutes. Filter, decompose the sulphides of selenium and tellurium with dilute hydrochloric acid and allow the liquid to stand in a warm place until the hydrogen sulphide is removed. Filter again, dissolve the sulphides in aqua-regia (nitric and hydrochloric acids), add .2 gram of potassium chloride, and evaporate the liquid to dryness on the steam plate. Take up with 90 per cent hydrochloric acid, heat to boiling, and precipitate with sulphur dioxide as in the first modification.

(c) *Precipitation by Stannous Chloride.*—When the selenium is largely in excess, a fairly good separation is most easily obtained by adding an excess of stannous chloride to the hot ferric chloride solution until the iron is decolorized, and allowing the covered beaker to heat until the liquid boils. Allow to settle overnight, if possible.

Prepare an asbestos felt by extracting with hydrochloric acid, igniting it, and then taking the “ignited” weight. Moisten the felt, dry in the oven, cool, and take a “dried” weight. After weighing the washed and dried precipitates of selenium or tellurium, or both, deduct the tare weight obtained by drying. Finally ignite the felt as a check.

A felt will occasionally suffer a slight loss in washing, in spite of the usual care. Selenium and tellurium are separated, if desired, by fractional precipitation with sulphur dioxide as in (a). Refer to the shorter combination method of the author, in connection with the arsenic and antimony determination (7, Chapter XII).

Zinc.—The separation of zinc is included and described with the method for cobalt (6) and nickel (7).

PART IV

CHAPTER XIV

ANALYSIS OF THE PRINCIPAL COMMERCIAL ALLOYS OF COPPER

Introduction. — This chapter presents the standard technical methods of one of the largest American brass companies. A description forwarded by Dr. Toisten of the Mansfeld Brass Works shows that the European methods for straight brass or bronze are practically identical with those to be described. Tests for nickel and spelter are also included, the latter being the one proposed as a standard by the Committee on non-ferrous alloys of the American Chemical Society. The analysis of antifriction metals and other special complex alloys is well described in another recent work.¹

COPPER IN ORDINARY BRASS

1. In the Absence of Tin. — One gram of drillings are weighed into a tall 200 c.c. beaker and dissolved in a mixture of 5 c.c. of sulphuric acid (d., 1.84), 2 c.c. of nitric acid (d., 1.42), and 18 c.c. of water. (As in previous chapters, all acids are understood to be of full strength and of the best grade, unless otherwise specified.) Dissolve the sample by heating, dilute the solution to about 120 c.c., and introduce a split platinum cylinder, having a total surface of 100 sq. cm. Electrolyze overnight with a current density of .5 ampere. The process may be hastened by the use of rotating electrodes and gauze cathodes, or preferably by the use of the Frary selenoid² described in Chapter I.

If the assays are finished by the slow process, wash off the electrodes and split watch-glass covers at the beginning of work the next day, and continue the current for about one hour longer. Test the electrolyte for the end-point by transferring about 1 c.c. of the liquid to a porcelain test plate and adding a few drops of fresh hydrogen sulphide water. Continue the elec-

¹ Price & Meade, *The Technical Analysis of Brass*.

² *J. Am. Chem. Soc.* **29**, 1592.

trolysis until there is no visible discoloration in the test. The cathode is removed quickly, plunged into a large beaker of water, dipped twice into alcohol, the excess shaken off, and the remainder burned, moving the cathode continually.

(Colorless denatured "pyro" alcohol of about 94 per cent strength is as safe to use as the best grade, at a fraction of the expense.) The use of dilute mixed acid avoids the necessity of evaporating to fumes, as the nitric acid remaining in solution secures uniformly good results.

LEADED BRASS CARRYING TIN

2. Technical Estimation of Tin. — (In this connection, refer also to alloys with iron and phosphorus.) To 1 gram of drillings or clippings add 10 c.c. of strong nitric acid. When the action has ceased, bring to a boil, add 50 c.c. of boiling water, and let stand until the metastannic acid has settled (about one hour), keeping the temperature just below the boiling point. It is important to keep this solution hot and filter hot, for if the liquid cools, the metastannic acid becomes partly soluble. Filter off the tin on a double 7 cm. paper, keeping the solution hot. It may be necessary to return the first portion of solution to the filter in order to have it run clear. J. T. Baker's ashless filters hold the tin better than any other tried. Some of the especially close grades of washed papers hold the moist metastannic acid properly but work so slowly that nothing is gained by using them. Wash the tin residue with boiling water and ignite, while moist, in a porcelain or platinum crucible, slowly at first and finally to the full heat of a Tirrell burner. The tin oxide must be ignited to a constant weight, and if more than 20 mg. in weight, the blast lamp is necessary for the final heating. Weigh as tin dioxide, SnO_2 factor, .7881.

Limitations. — The metastannic acid, obtained in this way, is free from copper, lead, zinc, and nickel, but will contain iron if it is present, also phosphorus. Also, the preceding method for tin is inaccurate in the analysis of an alloy containing iron in any considerable amount. Metastannic acid precipitated by nitric acid usually carries a part of the iron present. If the quantity of iron approximates that of the tin, nitric acid will render only a portion of the tin insoluble even with evaporation to hard dryness, but it is very unusual to find such conditions

in wrought brasses and bronzes. Ordinarily, iron is present in such small amounts as to be negligible in its effect. If much iron or phosphorus is present, proceed as described in the methods to follow: "Alloys containing tin with iron," and "Alloys containing phosphorus."

3. Technical Method for Lead. — To the filtrate from which the metastannic acid has been removed, or to the nitric acid solution of the alloy if no tin is present, add 40 c.c. of "lead acid," the preparation of which is given in the following paragraph. Evaporate to fumes and allow to cool. Take up with 35 c.c. of water, heat to boiling, then allow to cool and settle for five hours — better overnight. Filter off the lead sulphate on a Gooch crucible, wash with "lead acid," and remove the filtrate. Wash out the "lead acid" with a solution of equal parts of water and alcohol, finally with alcohol alone. Ignite and weigh the lead sulphate with the precautions noted in Fresenius's "Quantitative Analysis." (The factor for lead is .6831.)

Composition of Lead Acid. — This is a solution of one volume of sulphuric acid (d., 1.84) in seven volumes of water, saturated with lead sulphate. The solution is prepared as follows: 300 c.c. of sulphuric acid are poured into 1800 c.c. of water; 1 gram of lead acetate is dissolved in 300 c.c. of water and added to the hot liquid with stirring. The solution is allowed to settle for three or four days and poured off through a thick asbestos filter for use.

In dealing with small amounts of lead, it has been found in the precipitation of lead in (1:20) sulphuric acid (the best dilution) that the volume of solution is often so large in proportion to the lead present that a serious loss results. When lead acid is used, it is unnecessary to consider the solubility of the lead sulphate (that is, in technical foundry work), since the solution is always brought back to the same volume as the volume of lead acid originally added. Consequently, when the lead sulphate is filtered, no more lead remains in the filtrate than was originally added in the dilute sulphuric acid.

NOTE. — In a mutual investigation of a sample of complex "rolling-mill brass" for the U. S. Bureau of Standards, it has recently been determined that in an exact analysis of such material, the electrolytic deposition of lead from nitric acid

solution as the peroxide is more accurate than precipitation as sulphate. Copper and zinc salts have a slight solvent action on sulphate of lead, so that the assumption on which leaded acid is prepared and used is not strictly true, if the solution contains much copper and zinc. After the lead peroxide has been corrected for a trace of tin oxide and iron oxide which it may contain, the result is still a little higher by electrolysis.

4. Lead by Electrolysis.—Lead in leaded brass may also be determined by dissolving 1 gram in 10 c.c. of nitric acid and proceeding according to the exact electrolytic method **8**, described under the title "Impurities in Brass." One gram is the quantity used in works tests for the rapid determination of foundry mixtures.

5. Copper in Leaded Brass.—To the filtrate from the lead sulphate in **3**, add 3 c.c. of (1 : 1) nitric acid, bring to the proper volume, and electrolyze as in the first method for copper (**1**).

6. Zinc in Leaded Brass.—This element is usually taken by difference but may be precipitated as phosphate. The electrolyte from **5** may also be titrated as described in the "Analysis of German silver" (**23**).

EXACT DETERMINATION OF IMPURITIES IN BRASS

7. Lead as Sulphate, —in Absence of Tin.—When the amount of lead is small (less than .5 per cent), a 5-gram sample is dissolved in 25 c.c. of nitric acid, 120 c.c. of lead acid is added, and the liquid, if tin is absent, evaporated to fumes. Take up with 105 c.c. of water, boil, settle, and filter as described under "leaded brass." If tin is present, as is shown by a milkiness in the nitric acid solution after expulsion of nitrous fumes, add 125 c.c. of boiling water, allow the metastannic acid to settle, and filter off exactly as for the 1-gram sample. Add 120 c.c. of lead acid to the filtrate and proceed as above directed.

8. Exact Electrolytic Method for Lead.—For small amounts of lead the previous method has been largely superseded by the electrolytic, which is more exact (as noted in **3**), if corrections are made for traces of oxides of tin and iron contained in the anode deposit, when these elements are in solution with the lead and copper. If manganese is present in the alloy, it will also partially deposit with the lead.

Weigh a 5-gram sample into a 250 c.c. wide beaker. Dissolve in 25 c.c. of nitric acid and dilute to 150 c.c. with water. Electrolyze with current reversed, i.e., with the sheet electrode for the anode,—first, for one-half hour at .1 ampere per solution and then three hours at .5 ampere. Test by exposing a clean surface to the liquid. When this test shows the deposition to be complete, remove the electrode, wash with water, and then with alcohol. Dry in an oven at least half an hour, and finally cool and weigh as lead dioxide. For lead the factor .8643 is used, following the results of Dr. E. F. Smith and others. If the lead is excessive, it is best to employ a gauze electrode to prevent flaking of the deposit.

In Presence of Tin.—Dissolve 5 grams in 25 c.c. of nitric acid, dilute with 125 c.c. of boiling water, and filter off the metastannic acid exactly as in 2. In very exact work, dissolve the tin compound in hot ammonium sulphide containing ammonium chloride, filter, dissolve the washed black sulphides from the paper, and return them to the copper solution. In the solution determine the lead as already directed. The deposit may be removed after weighing by the solvents described under "Electrolysis of Lead in Copper" (page 222). To obtain the correct weight of the platinum, it should be ignited and weighed again after cleaning, as it loses weight perceptibly during electrolysis.

9. Iron, Exact Method.—Dissolve 5 grams of brass in 25 c.c. of nitric acid, boil off nitrous fumes, dilute, and add ammonium chloride and ammonia in excess. Boil, filter on an S. & S. black ribbon paper, wash with dilute ammonia and then with hot water. Dissolve the iron precipitate in hot (1:1) hydrochloric acid and reprecipitate with ammonia. Dissolve the ferric hydroxide after the second precipitation in hot (1:4) sulphuric acid on the filter, washing out thoroughly with dilute acid and hot water. Add 40 c.c. of (1:1) sulphuric acid, pass through a Jones' reductor (or add hydrochloric acid and decolorize with one drop of stannous chloride in excess). Then titrate with potassium permanganate. For the use of the reductor, consult "The Chemical Analysis of Iron" by Blair. If the reduction is made by stannous chloride, add 5 c.c. of a saturated solution of mercuric chloride and 10 c.c. of titrating solution to secure a good end-point. (See 7, Chapter V.) For brass, German silver,

and spelter make the permanganate solution with .3 gram of the crystals per liter, and standardize against .015 to .018 gram of pure iron wire. One c.c. of solution then equals about .0005 gram of iron.

In Presence of Traces of Tin. — In such a case, the insoluble metastannic acid must be removed as in 8, and the filter and contents extracted with about 30 c.c. of warm yellow ammonium sulphide, containing 1 gram of ammonium chloride. The iron sulphide, thus obtained, is dissolved in dilute nitric acid and returned to the original solution of the alloy.

ALLOYS CONTAINING TIN WITH IRON

(Examples: Manganese Bronze, Phospho-Bronze)

10. Copper Assay, for Control of Mixtures. — Dissolve a 1-gram sample in 10 c.c. of nitric acid, boil, wash down, and bake thoroughly. Moisten with nitric acid, dilute, boil, allow to settle, and filter off all possible tin oxides, exactly as for brass (2). The filtrate contains some of the tin, notwithstanding the baking. Add to the filtrate 10 c.c. of (1:1) sulphuric acid and evaporate to strong fumes. Dilute to about 120 c.c. and electrolyze as usual for copper. When the deposition is complete, the solution may show a yellow color on the spot plate with hydrogen sulphide water, due to the tin present in solution, but there should be no darkening of the cathode copper. If darkening occurs, the cathode deposit may be dissolved in nitric acid and the tin removed easily (since iron is no longer present). The copper may then be reprecipitated. This purification is seldom necessary in routine work.

11. Exact Electrolysis for Copper. — The next modification was developed by the author in analyzing the "Rolling Mill Brass" for the U. S. Bureau of Standards. Dissolve 5 grams of drillings in 25 c.c. of nitric acid and 75 to 125 c.c. of water, then filter off and purify the metastannic acid with warm yellow ammonium sulphide exactly as in 8. Dissolve the trace of copper sulphide, etc., in 5 c.c. of nitric acid, diluted with 2 parts of water, and return it to the main solution which has been already treated with 10 c.c. of sulphuric acid and evaporated to fumes. The diluted solution, which contains traces of dissolved tin, should then be filtered from the lead sulphate.

Five cubic centimeters of nitric acid should be present in the

solution. It is possible to deposit the copper and lead simultaneously from a pure nitric acid solution, if preferred, the one on the cathode, and the other on the anode, which should also be a cylinder, or dish.

The trace of tin in the first deposit of copper is easily removed by standing the cathode in a tall beaker and adding 40 c.c. of the "acid mixture" used for the electrolytic assay of refined copper (2, Chapter XI). Dilute with sufficient water to cover the plate, cover the beaker with a glass perforated with a small hole for the stem of the electrode, and allow to stand on the steam plate until dissolved. Repeat the electrolysis. As the second electrolyte is free from iron, the last deposit will be free from tin, and the second electrolyte may be subsequently combined with the first to obtain a complete recovery of the tin.

Rapid Assay.—Use a rotating anode, or better, the Frary solenoid, observing the precautions indicated in the rapid assay of refined copper (Chapter XI):—Current requirement, 4 to 4.5 amperes per square decimeter of immersed cathode surface.

12. Tin and Iron in Bronze (Special Method).—This modification was reported by Bassett and Merrill in the assay of U. S. standard "Rolling Mill Brass." Five-gram samples should be treated, if results are to be reported to .01 per cent. Otherwise, dissolve a separate 1-gram sample in 10 c.c. of hydrochloric and 5 c.c. of nitric acid. Dilute, and make a double precipitation with ammonia to separate tin and iron from the copper. Dissolve the oxides the first time in hot (1:1) hydrochloric acid and the next time in very hot (1:2) sulphuric acid. Wash very thoroughly with this acid. Dilute, filter off any trace of lead sulphate, and saturate the solution with hydrogen sulphide. Filter off the tin sulphide, wash, and ignite to stannic oxide, SnO_2 , as described under "phospho-bronze." Heat the filtrate from the tin sulphide to expel the hydrogen sulphide, oxidize with nitric acid, and add ammonium chloride and ammonia in excess. Boil, filter, wash the ferric hydroxide, dissolve in dilute sulphuric acid, and titrate as in method 9 for iron in brass. T. J. Demorest has recently devised a new scheme for complex alloys which deserves a trial (see reference¹).

13. Tin in Phospho-Bronze.—In alloys of this kind, copper, zinc, and tin are determined in one sample. The metastannic

¹ *J. Ind. and Eng. Chem.* 5, 842.

acid (containing phosphorus) is filtered off exactly as in the analysis of brass (2), and the copper and zinc estimated as described.

The paper with the tin precipitate is extracted in a small beaker with ammonium polysulphide and ammonium chloride, then filtered and the residue washed thoroughly with dilute yellow ammonium sulphide. The lead and iron sulphides are filtered from the dissolved tin, and the polysulphide solution is made acid with acetic acid (instead of sulphuric), heated to boiling, and filtered. The precipitated tin sulphide is ignited directly with the moist paper to stannic oxide, SnO_2 , taking care to ignite to constant weight. This ignition must proceed slowly and carefully until the sulphur is roasted off. The sulphur should not be allowed to burn, for some tin sulphide might be volatilized. The ignition is best started in a porcelain crucible, placed upright in a hole in a piece of asbestos board in which it fits tightly near the top. When the sulphur is expelled, the crucible is ignited in a slanting position upon a triangle. If the tin oxide weighs over 20 mg., finish with the blast lamp.

Impure metastannic acid may also be purified by igniting, mixing with three parts of sodium carbonate and three parts sulphur, and fusing in a porcelain crucible. Some chemists prefer to place the small crucible inside a larger one.¹ The fusion is taken up with hot water, boiled to insure complete precipitation of foreign sulphides, filtered, and the tin finally separated with acetic acid as above described.

PHOSPHORUS

14. By Titration.—Dissolve a separate 1-gram sample in a casserole by an acid mixture containing two parts of hydrochloric acid and one of nitric acid. Evaporate to dryness. Moisten with hydrochloric acid, evaporate to dryness again, and heat to dull redness. (This removes most of any arsenic present.) Moisten with hydrochloric acid, add water and about 3 c.c. of strong ferric chloride solution, make alkaline with ammonia, boil and filter, wash with dilute ammonia, and then with hot water. Dissolve the iron precipitate (which carries the phosphorus) in hot (1:1) hydrochloric acid, dilute, and satu-

¹ Blair, *The Chemical Analysis of Iron*, 7th Edition, p. 95; *Year Book Amer. Soc. Testing Materials* (1915).

rate the liquid with hydrogen sulphide. Filter off the tin and copper sulphides, oxidize the filtrate with nitric acid, and reprecipitate with ammonia. Dissolve the ferric hydroxide with hot (1:4) sulphuric acid into an Erlenmeyer flask. Add ammonia to the solution in the flask until it is alkaline, make slightly acid with nitric acid, add ammonium molybdate solution, and proceed as in the determination of "phosphorus in steel."

The contributing chemists employ the ferric-alum modification of the permanganate titration, adopting the same strength of solution as for iron or manganese, — 3 grams of crystals per liter. The "yellow precipitate" may be dissolved in ammonia, if preferred, the solution made acid, then alkaline, and treated with excess of magnesia mixture.

MANGANESE

15. Manganese in Alloys. — If the sample contains tin, dissolve 5 grams in 25 c.c. of nitric acid, dilute with 125 c.c. of boiling water, and filter off the metastannic acid as described under "Brass" (2 to 8). If tin is absent, dissolve as before without filtration. In either case, evaporate the solution to a sirup in a tall 500 c.c. beaker, add 100 c.c. of nitric acid and 5 grams of potassium chlorate, and proceed as in William's modification of Ford's method.¹

In this process, the first precipitate of manganese dioxide may contain a little impurity, which would require re-solution and reprecipitation with nitric acid and potassium chlorate. The ferrous ammonium sulphate solution should be composed of 100 grams of the crystals, 50 c.c. of sulphuric acid (d., 1.84), and 2000 c.c. of water. Usually, 10 c.c. of solution are sufficient to dissolve the precipitated manganese dioxide. The potassium permanganate contains 3 grams of the crystals per liter, or ten times the strength used for iron in brass (9). It is standardized against .10 to .12 gram of pure iron wire. To estimate the manganese, dissolve the dioxide in 10 c.c. of the ferrous sulphate solution, protecting it from the air. Immediately titrate back the unused ferrous salt with the permanganate. $\text{Fe} \times .4919 = \text{Mn}$.

16. Gravimetric Method. — Manganese may also be determined by Ford's method,¹ dissolving the sample and oxidizing the manganese as in the previous method. The first precipitate

¹ Blair, *Chemical Analysis of Iron*, 7th Edition, 114-118.

should be dissolved and reprecipitated for purification. After dissolving the purified dioxide, the manganese is finally thrown down by a large excess of ammonium phosphate in a boiling, slightly ammoniacal solution. Add the precipitant slowly to the hot liquid, stirring rapidly. Continue heating and stirring until the crystals assume the true color and silky appearance. Filter, wash, and dry the precipitate; then ignite carefully to avoid any reduction. Use the conversion table of Chapter XVI.

The sodium bismuthate method is also very exact. (See method 25, Chapter VI.)

ALLOYS CONTAINING A LITTLE NICKEL

17. Nickel. — In alloys where there is a relatively low ratio of nickel to zinc (not over 1 to 15), a method is desirable which will permit a quick and accurate separation of the small amount of nickel from the large amount of zinc, with the final determination of the nickel by electrolysis.

In the *complete analysis* of any complex alloy, the filtrate from tin and iron is taken for the separation of nickel and zinc. Precipitate the nickel by dimethyl glyoxime from the hot, slightly ammoniacal filtrate according to the *special method* below, and follow with the estimation of the zinc in the filtrate from the nickel. The sodium potassium tartrate is omitted, as no iron is present.

18. Special Method for Nickel. — Dissolve a special 1-gram sample exactly as in the determination of copper in brass (**1, 5**), and remove the copper by electrolysis. A little copper in the electrolyte does no harm. Concentrate the solution to about 100 c.c., add 1 gram of ammonium chloride, then 10 c.c. of a 20 per cent solution of sodium potassium tartrate. Neutralize with ammonia, adding about 2 c.c. in excess, and then stir in 5 c.c. of a 1 per cent alcoholic solution of dimethyl glyoxime for each per cent of nickel. This method is due to O. Brunck and Tschugaeff.¹ Allow the solution to stand for one-half hour, filter, and wash with very dilute ammonia. Dissolve the red precipitate in hot (1:1) hydrochloric acid, add 10 c.c. of (1:1) sulphuric acid, and evaporate to strong fumes of sulphur trioxide. Dilute, neutralize with ammonia, and add 20 c.c. in excess; electrolyze

¹ *Zeit. Angew. Chem.* **20**, 834 and 3844.

with a current of .3 ampere per solution. Test for the end-point with fresh hydrogen sulphide water, as in the "determination of copper in brass" (1 and 5).

NOTE. — The Frary solenoid may be used to advantage with a current of 4 amperes per solution. With this rapid circulation and heavy current the time is reduced to one hour.

SULPHUR IN BRASS OR NICKEL ALLOYS

19. Precipitation as Barium Sulphate. — Weigh duplicate 10-gram samples of drillings into a 600 c.c. tall-lipped beaker. Add about .5 gram of pure sodium carbonate. Cover and then add 50 c.c. of nitric acid. When the action has ceased, boil off red fumes, evaporate off the bulk of the solution, and allow to bake overnight at the temperature of the steam bath. Fill to the lip with warm water. There should be present a layer about $\frac{1}{4}$ inch (6 mm.) thick, composed of basic salts of copper. Add 3 c.c. of (1 : 1) nitric acid and electrolyze, placing the beaker in a large Frary solenoid, or rotary device. The lead may be removed at the anode as copper is taken out at the cathode. When the copper is gone, evaporate to small volume, cover the beaker, add 75 c.c. of hydrochloric acid, and boil down to a small volume. Add 75 c.c. more hydrochloric acid and evaporate to dryness. Take up with water, make alkaline with ammonia, and dilute to the lip of the beaker.

Then proceed to remove the nickel and zinc by electrolysis, using a large iron cathode and the Frary rotary device. When the solution is colorless, wash down the electrodes; remove them, and heat the solution to boiling. Let settle and filter through an 11 cm., black ribbon paper into a 600 c.c. tall beaker. Make the solution acid with hydrochloric acid and evaporate until the ammonium chloride starts to crystallize. Cover and add 50 c.c. of nitric acid. Boil down to small bulk; add 25 c.c. of hydrochloric acid and boil until no more chlorine is evolved. Wash down the cover and evaporate to dryness to dehydrate any silica present. Moisten with hydrochloric acid and take up with 20 c.c. of hot water. Filter into a small beaker. Heat the filtrate to boiling, add 5 c.c. of 5 per cent barium chloride solution, drop by drop, with stirring. Allow to settle at least five hours, filter on a small ashless paper, and wash with hot

water. Ignite cautiously in a small porcelain, or platinum, crucible, and then heat to bright redness for twenty minutes. Cool and weigh the barium sulphate. $\text{BaSO}_4 \times .1374 = \text{sulphur (S)}$.

NOTE. — The utmost precautions should be taken to prevent contamination with sulphur in any form. Avoid gas-heating, except by gasoline gas. Run a blank analysis; that is, take a 600 c.c. beaker, add to it all the reagents, and subject the contents to the same operations as the samples of drillings, and at the same time. Deduct any barium sulphate obtained from the result of the actual assay. If this blank amounts to .0020 gram, it is a sign of poor work and the analysis should be repeated. Wash out all beakers, funnels, etc., with distilled water before use.

ZINC IN BRASS AND BRONZE

20. Volumetric Method. — The filtrate from the iron precipitation, or from the nickel separation when that element is present, is taken for the determination of zinc. In brass works, the custom is to employ rapid titration. Add 20 c.c. of nitric acid (d., 1.42) to the filtrate from the nickel precipitation. Boil, add some ferric chloride, citric acid, and ammonia; then titrate with potassium ferrocyanide exactly as directed in the analysis of nickel alloys (23).

21. Gravimetric Method. — For an occasional analysis, or in umpire work, some chemists prefer a precipitation and ignition of zinc phosphate. The filtrate from the nickel separation (16) may be used after boiling out the alcohol, or a new sample may be treated as follows: Precipitate lead and copper from the acid solution of the sample on sheet aluminum according to (25) Chapter VI. To the final solution (volume about 50 c.c.) add 50 c.c. of a 10 per cent solution of ammonium phosphate, make just alkaline to litmus, then acid with 1 c.c. of acetic acid in excess. Heat just below boiling for about an hour. This treatment should cause the zinc to become granular. Allow to settle, filter, wash with hot water, and dry the substance. Char the filter separately, ignite the phosphate with care, cool the crucible, and weigh the precipitate. (To obtain the weight of the zinc, multiply the weight of the ignited pyrophosphate, $\text{Zn}_2\text{P}_2\text{O}_7$ —, by .4289.

ANALYSIS OF NICKEL ALLOYS

(Example, German Silver, Monel Metal.)

22. Copper. — The copper is determined as in brass. In arranging the cathode, allow it to project about $\frac{1}{8}$ inch above the solution. When the copper is apparently all precipitated, wash down the cover glasses and sides of the beaker, which will cause the solution to cover the cathode. If no sign of copper is seen on the clean platinum, it indicates that the deposition is complete. If copper does appear, the electrolysis must be continued several hours, or until the solution polarizes and gas bubbles come off freely from the cathode.

23. Zinc. — After removing the copper as above, concentrate the solution to about 75 c.c. and transfer to a tall 500 c.c. beaker, make just alkaline with ammonia, then acid by adding 2 c.c. of formic acid (d., 1.2), then add enough ammonia to barely restore the blue color. Finally, add formic acid of the same density in the proportion of 38 c.c. for every 200 c.c. of final volume of solution. Heat to boiling and pass a rapid stream of hydrogen sulphide gas into the liquid for fifteen minutes, using a fine jet tube. Start the gas before putting the tube into the liquid, for if the interior of the tube becomes wet with the solution, nickel sulphide will deposit on the inside of the tube. Filter off the pure white zinc sulphide and wash with hot water; dissolve in hot dilute hydrochloric acid; filter off the sulphur and wash the paper. Any slight black residue may be dissolved in a few drops of nitric acid and returned to the nickel solution. The nickel solution should then be heated up and more hydrogen sulphide passed to make sure that the zinc is all out. To the hydrochloric acid solution of the zinc sulphide, add nitric acid and boil to oxidize the hydrogen sulphide. Cool and add 3 c.c. of a strong solution of ferric chloride, 20 c.c. of a saturated citric acid solution, and ammonia to make distinctly alkaline. A very large excess of ammonia should be avoided. Heat this solution, which should have a volume of from 250 to 300 c.c., to boiling, and titrate with potassium ferrocyanide solution.

Titration. — To determine the end-point with ferrocyanide, the pits in the porcelain test plate are filled with a 50 per cent acetic acid solution. When the titration is nearly completed (which may be judged from the conditions), two drops are taken

out and added to the acetic acid in one of the pits. This gives a slight greenish tint, and a few drops more of the ferrocyanide are added and another portion taken out. This is continued until the end-point, which is a distinct blue, is reached. On making acid with the two drops of acetic acid, a Prussian blue is not formed until all the zinc has been precipitated as ferrocyanide. It requires about $\frac{1}{2}$ c.c. of the ferrocyanide to give a distinct end-point in 250 c.c. of solution containing no zinc. The ferric chloride is added as an indicator, but if the solution contains sufficient iron, as it does in the case of certain zinc ores, the addition of this iron is not necessary. Small amounts of aluminum, lime, and magnesium make no difference in this titration.

The correction for the blank in getting the end-point must be made by the operator. This titration is difficult for an inexperienced operator, but for one used to the method it is one of the most accurate methods for the determination of zinc and is both rapid and easy to handle. It is accurate within about .2 per cent and the experienced operator can check his own results within about .1 per cent. This titration must be carried out in every case in exactly the same manner as the standardization.

The potassium ferrocyanide solution is made up by dissolving 80 grams of the salt in 2500 c.c. of water and standardizing against a solution of pure metallic zinc. The potassium ferrocyanide should be allowed to stand at least six weeks before use; in that time changes which occur in such solutions will have completed themselves, and the standardization value will remain permanent. This value is ascertained by weighing out 2 grams of zinc, dissolving the metal in nitric acid, and making up to 1000 c.c. Take 100 c.c. of the solution, add 5 c.c. of nitric acid, 3 c.c. of ferric chloride, and 20 c.c. of saturated citric acid solution, dilute, and make distinctly alkaline with ammonia. The final volume should be 250 c.c. Boil and titrate while boiling hot with the ferrocyanide solution and figure the zinc equivalent.

24. Alternative Titration for Zinc.— This alternative method is based on the paper entitled "A Proposed Standard Method," written by Frank G. Breyer.¹

¹ 8th Int. Cong. of Appl. Chem. **1**, 162.

Proceed as in **23** until the pure white zinc sulphide has been filtered off and washed with hot water. Return the paper and precipitate to the original 500 c.c. beaker and add 20 c.c. of (1:1) hydrochloric acid. When the zinc sulphide is dissolved, filter off the paper together with some sulphur and possibly a little nickel sulphide, which may be treated as directed in **23**. Boil the solution, containing the zinc, slowly for about fifteen minutes to expel hydrogen sulphide; cool and wash down. Add 13 c.c. of ammonia (d., .90), and if the solution is not then alkaline, make it so by cautious addition of ammonia. There must be enough hydrochloric acid present to neutralize at least the above amount of ammonia. Make the solution barely acid again with hydrochloric and add 3 c.c. of concentrated acid in excess. Add 1 c.c. of a solution of ferrous sulphate containing 3 grams of the salt per liter, dilute nearly to 200 c.c., heat almost to boiling, and titrate with potassium ferrocyanide. The ferrocyanide employed for this titration contains 44 grams of the potassium ferrocyanide and .3 gram of potassium ferricyanide per liter and is prepared at least six weeks before use. The end-point is a sharp change in the color of the solution from a turquoise blue to a "pea green," and with several more drops to a "creamy yellow." This end-point occurs a little sooner than the one with uranium nitrate, and is easier to use, as the change is seen directly in the solution. If the sample does not contain at least 3 per cent of zinc, which can be estimated by the appearance of the zinc sulphide, 20 c.c. of a standard solution, containing 6 grams of pure zinc in 2000 c.c., are added from a pipette just after the solution to be titrated has been boiled to expel the hydrogen sulphide, and the solution is then made ready for titration as described above. This addition of zinc is necessary in order to obtain a good end-point.

The ferrocyanide solution is standardized in the following manner: Six grams of zinc are dissolved in 40 c.c. of hydrochloric acid in a 2-liter flask, the solution made up to the mark with the usual precautions, and 100 c.c. taken for titration. Add 10 c.c. of hydrochloric acid (d., 1.2) and 13 c.c. of ammonia (d., .90) If the solution is not then alkaline, it is made so with further addition of ammonia. Acidify again with hydrochloric acid, adding the acid drop by drop, and an excess of 3 c.c. of the strong acid. After addition of 1 c.c. of the ferrous

sulphate solution previously described, the solution is diluted nearly to 200 c.c., is heated almost to boiling, and is treated as described above.

NOTE, on *Gravimetric Method*.—Any laboratory making an occasional analysis only, will find it less work to employ a modification of the Waring method described under “Zinc in ores” (17, Chapter VII), and in the “Analysis of Brass” (21, this chapter).

25. Nickel in German Silver.—Nickel is usually taken by difference after the iron has been determined. If the estimation of nickel is required, after filtering out the sulphide of zinc, evaporate the nickel solution to dryness, then cover the beaker, add 25 c.c. each of hydrochloric and nitric acids, and heat to destroy the formates. This oxidation with aqua-regia is repeated until all the formates are destroyed. The small amount of nickel sulphide, which is brought down by the zinc sulphide and which is filtered off from the hydrochloric acid solution of the zinc sulphide, must also be added. After destroying the formates, add 3 c.c. of sulphuric acid and evaporate to strong fumes. Dilute, neutralize with strong ammonia, and add 20 c.c. of strong ammonia in excess, making about 125 c.c. in all. Electrolyze with a current of .3 ampere per solution. Test the solution for the end-point by fresh hydrogen sulphide water as in the case of copper.

Rapid Electrolysis.—The author has found the Frary solenoid to be well adapted to the deposition of nickel. The nickel ammonium sulphate is a better conductor of the current than a neutral solution, hence the liquid should contain the ammonium sulphate and be kept strongly alkaline. Current 4 amperes per solution. In very accurate work, the deposit should be dissolved in nitric acid, the cold dilute solution treated with 10 c.c. of hydrogen sulphide water, filtered, and the residue washed, ignited, and weighed. If no copper is found, the residue may be assumed to be platinum carried over from the anode by the strong current.

26. Iron in German Silver.—Dissolve 2 grams of the alloy in 15 c.c. of nitric acid and proceed exactly as in the determination of iron in brass.

27. Carbon by Combustion.—Place 5 grams of drillings in a

500 c.c. beaker and add 300 c.c. of a saturated solution of copper-potassium chloride and 22.5 c.c. of hydrochloric acid (d., 1.19). Stir and allow to stand in a warm place overnight, or, if necessary, hasten the operation by a mechanical stirrer. Filter on a platinum crucible (made up with ignited asbestos), wash thoroughly with dilute hydrochloric acid and finally with hot water to remove all chloride. Place the Gooch crucible inside a Shimer crucible, ignite in a combustion train, and determine the carbon in exactly the same way as "carbon in steel." It is absolutely essential that the beakers and solutions shall be protected from dust by double coverings until the carbon has been transferred to the combustion apparatus.

REFINED NICKEL

28. Electrolytic Assay. — Weigh duplicate 2-gram samples into 250 c.c. beakers, cover, and dissolve in 30 c.c. of (1 : 1) nitric acid. Dilute, add about 5 grams of ammonium chloride, and make alkaline with ammonia. Heat carefully to boiling and filter off the ferric hydroxide on a small "black ribbon" S. & S. paper, receiving the filtrate in a tall 500 c.c. beaker. Wash with dilute ammonia and with hot water. Dissolve the precipitate into the original 250 c.c. beaker with a little hot (1 : 1) hydrochloric acid. Reprecipitate with ammonia, filter, and combine this filtrate and washings with those from the first precipitation. Stand this solution on a hot plate to concentrate and evaporate off the excess of ammonia. Cover and add 50 c.c. of a mixture of equal parts of nitric and hydrochloric acids, and boil to small volume. Cool, add 20 c.c. of (1 : 1) sulphuric acid, and repeat the treatment with nitric and hydrochloric acids, until the ammonium salts are entirely expelled. Wash down, remove cover glass, and allow the solution to evaporate to strong fumes. Dissolve the nickel sulphate in water, neutralize with ammonia (d., .90) and add 20 c.c. in excess. Electrolyze overnight with a current of .25 ampere per solution. Test with hydrogen sulphide as in preceding methods. The cathode, after burning off the alcohol, is baked in the oven for one hour at about 105° C. The deposit is nickel plus cobalt plus copper. No attempt is ordinarily made to determine the nickel and cobalt separately. Copper is estimated on a separate sample, and the amount found is subtracted from the total amount of the copper + nickel + cobalt.

Iron, if present, causes slightly high results, probably being brought over mechanically as hydroxide and weighed as oxide. Electrolyze with a gauze cathode and a current of 5 amperes per solution for $1\frac{1}{2}$ hours if preferred, using some rotary device. This deposit may be purified as outlined in the last paragraph of 25.

29. Special Assay for Copper. — Dissolve a 5-gram sample in a casserole, using 50 c.c. of (1 : 1) nitric acid; add 20 c.c. of (1 : 1) sulphuric acid and evaporate to strong fumes. Add about 20 c.c. of water, heat until nickel sulphate is dissolved, add about 10 grams of ammonium chloride, and saturate with hydrogen sulphide gas. Filter off the copper sulphide (which may contain a little nickel), place the filter and contents in a tall 200 c.c. beaker, add 10 c.c. of (1 : 1) sulphuric and 25 c.c. of strong nitric acid, then boil down to strong fumes. If the filter is not destroyed leaving a clear solution, more nitric acid may be added, and the solution boiled down to fumes again. Dilute to 120 c.c., add 3 c.c. of (1 : 1) nitric acid, and electrolyze as usual for copper.

30. Iron in Refined Nickel. — Dissolve a 2-gram sample in 30 c.c. of (1 : 1) nitric acid, dilute, add ammonium chloride and ammonia in excess, and proceed exactly as in "the estimation of iron in brass."

STANDARD ANALYSIS OF ZINC SPELTER

31. Classification. — The sub-committee on alloys of the American Chemical Society recommends a method of testing spelter, which has been elaborated from those originally proposed by Elliot and Storer¹ and Price,² and which closely agrees with the procedure of the American Society for Testing Materials.³ The sampling of spelter is described in 36, Chapter II.

Spelter ordinarily used for brass and similar alloys is usually considered in three grades: A, "High Grade"; B, "Intermediate"; C, "Brass Special," according to the amount of lead and other impurities present. A fourth grade, D, "Prime Western," contains more impurities than the three grades preced-

¹ *Mem. Acad. Arts and Sciences*, 8, Pt. 1, May 20, 1830.

² *Chem. Eng.* 9, 4.

³ *Year Book*, 1914, page 384; also personal communications.

ing. In 1916, a new "Selected Grade," with .80% lead, has been proposed.

HIGH LIMITS.

Grade	A. High	B. Interm.	C. Special	D. Western
	Per cent	Per cent	Per cent	Per cent
Lead.....	.07	.20	.75	1.50
Iron.....	.03	.03	.04	.08
Cadmium.....	.05	.50	.75	?
The sum of lead, iron and cadmium shall not exceed	.10%	.50%	1.20%	?
Aluminum.....	.00	.00	.00	?

ANALYSIS

32. Lead, by "Lead Acid" Method. — Weigh into a 350 c.c. beaker 25 grams, 15 grams, 10 grams, or 5 grams of sawings or drillings, according to whether the spelter is of grade A, B, C, or D, respectively, and add, according to weight of sample, 300 c.c., 180 c.c., 120 c.c., or 60 c.c. of "lead acid." For preparation of lead acid, see note. When all but one gram of zinc is dissolved, filter on a close paper and wash out the beaker twice with "lead acid" from a wash bottle. Wash the metallics back from the filter to the original beaker with water and dissolve in a little hot (1:1) nitric acid. Add 40 c.c. of lead acid, and evaporate to strong fumes of sulphuric acid. When cool, add 35 c.c. of water (which is the quantity of water evaporated from the lead acid) and heat to boiling. Add the first filtrate (containing most of the zinc and possibly a little lead), stir well, and settle at least five hours, filter, wash with lead acid, then with a solution of equal parts of alcohol and water and finally with alcohol alone. Ignite, and weigh the lead sulphate as usual.

NOTE. — "Lead acid" is a solution of one volume of sulphuric acid (d., 1.84) in seven volumes of water, saturated with lead sulphate. It is prepared as directed in the first part of this chapter (3), under the method for "lead in brass."

33. Lead, by Electrolysis. — Weigh out 8.643 grams of the sample into a 400 c.c. beaker and add sufficient water to cover the sample. Then 30 c.c. of concentrated nitric acid (d., 1.42) are added gradually and cautiously until solution is complete,

and the solution is boiled for a few minutes to dispel the nitrous fumes. Wash off the cover glass and sides of the beaker and transfer the liquid to a 200 c.c. electrolytic beaker. Dilute to 125 c.c. and electrolyze with a current of five (5) amperes. The time required for the electrolysis is from $\frac{1}{2}$ to $\frac{3}{4}$ of an hour, depending on the amount of lead present in the sample. Solutions are tested for complete precipitation of lead by washing down the cover glasses and sides of the beaker, so that the depth of the solution is increased about $\frac{1}{2}$ inch (1.2 mm.). The current is then continued for fifteen minutes and if the newly exposed surface is still bright, the lead is completely deposited. The anode is then washed three or four times with distilled water, once with alcohol; then dried in an oven at 210° C. for $\frac{1}{2}$ hour and weighed.

The weight of the lead dioxide, PbO_2 , in milligrams, divided by 100 will give the percentage of lead. The dioxide deposit can be readily removed by covering the anode with dilute nitric acid and inserting a rod of copper.

The electrodes recommended by the Committee are cylinders of platinum gauze, 48 meshes to the linear inch (or 18 per cm.). The anodes are $1\frac{1}{4}$ inches (31.6 mm.) in diameter and of equal height, with a stem $4\frac{1}{4}$ inches (108 mm.) long of 16-gauge wire, making the total height $5\frac{1}{2}$ inches (or 14 cm.). The cathodes are $\frac{1}{2}$ inch (12.7 mm.) in diameter, but having the same height and length of wire stem as the anodes.

34. Iron.—Weigh 25 grams of zinc into a tall 700 c.c. beaker and dissolve cautiously in 125 c.c. of nitric acid. Boil, dilute, add considerable ammonium chloride, and then ammonia until the white zinc salts have dissolved. Boil, let settle, and filter on a 11 cm. S. & S. "black ribbon" filter paper. Wash with dilute ammonia and with hot water. Dissolve the precipitated ferric hydroxide with hot (1:4) sulphuric acid, add 40 c.c. of (1:1) sulphuric acid, pass through a Jones reductor, wash first with 150 c.c. of water, then with 100 c.c. of water, and titrate with permanganate.

The potassium permanganate solution contains .2 gram of the crystals per liter. One c.c. of the permanganate will equal .000334 grams of iron. The solution is standardized against sodium oxalate, whose correctness has been guaranteed by the maker. Weigh out duplicate samples of sodium oxalate, weigh-

ing .0200 gram. This will take between 49 and 50 c.c. of the permanganate solution. To convert sodium oxalate to iron, use the factor .8334. Run through a blank using the same amounts of water and acid and deduct from the titration.

NOTE. — If before passing the solution through the reductor, a large amount of lead sulphate is present, it is well to filter it off to prevent it from clogging the reductor.

35. Cadmium. — Weigh 25 grams of drillings into a tall beaker; add 250 c.c. of water and 55 c.c. of concentrated hydrochloric acid and stir. When the action has almost ceased, add more acid with stirring, using about 2 c.c. at a time, and allowing to stand after each addition of acid, until finally all but about 2 grams of the zinc have been dissolved. About 60 c.c. of acid in all are usually required; it is best to allow the first 55 c.c. of acid to act overnight. Filter, first transferring one of the undissolved pieces of zinc to the filter, and wash a couple of times with water. Discard the filtrate. Wash the metallics on the filter paper back into the 500 c.c. beaker, cover, and dissolve in nitric acid. Transfer to a casserole, add 20 c.c. of (1:1) sulphuric acid and evaporate to fumes, take up with about 100 c.c. of water, boil, cool, and let settle for several hours (best overnight). Filter off the lead sulphate on paper, wash with water, retain the filtrate, and discard the lead sulphate. Dilute the filtrate to 400 c.c., add about 10 grams of ammonium chloride, and pass hydrogen sulphide into the liquid for one hour. It is occasionally necessary to start the precipitation of the cadmium sulphide by the addition of one or two drops of ammonia to the dilute solution. Allow to stand until settled, filter off the impure cadmium sulphide in a loose-bottomed Gooch crucible; remove the cadmium sulphide by carefully punching out the bottom into a 200 c.c. tall beaker. Wipe off any adhering cadmium sulphide, using a little asbestos pulp, add 60 c.c. of (1:5) sulphuric acid, and boil for one-half hour. The dilute acid dissolves cadmium and zinc sulphides, but not copper or lead sulphides. Filter and dilute to 300 c.c., add 2 grams of ammonium chloride, and precipitate with hydrogen sulphide in order to get rid of traces of zinc. Let settle, filter, and transfer to a platinum dish, cover, and dissolve in (1:3) hydrochloric acid.

Then the sulphide remaining on the filter paper is also dissolved by hot (1 : 1) hydrochloric acid, and is added to the solution in the platinum dish. A little sulphuric acid is added and the solution is evaporated to strong fumes of sulphuric acid. It is diluted with water, a few cubic centimeters of strong nitric acid are added to oxidize any shreds of filter paper, and the solution is again evaporated to sulphuric acid fumes. The excess of sulphuric acid is removed by heating the dish cautiously, and finally heating nearly to redness, and the cadmium is weighed as sulphate.

36. Cadmium by Electrolysis.—Proceed as above until the purified cadmium sulphide has been dissolved in hydrochloric acid. Then oxidize with nitric acid and filter from sulphur. Transfer the solution to 200 c.c. electrolytic beaker, add a drop or two of phenolphthalein and then pure sodium or potassium hydroxide solution until a permanent red color is obtained. A strong solution of pure potassium cyanide is then added with constant stirring until the precipitate of cadmium hydroxide is completely dissolved. Avoid using an excess of the potassium cyanide. Dilute the solution to 150 c.c. and electrolyze with a current of 5 amperes, using the same size gauze electrodes as in the "lead determination." Time, one to two hours. The solution should always be tested for cadmium as follows: raise the liquid in the beaker and then note after twenty minutes the newly exposed surface of the electrodes. If still bright, the cadmium is completely deposited. Next wash the electrodes with distilled water and then with alcohol. Dry at 100° C., cool and weigh. The increase is metallic cadmium.

37. Special Titration for Lead.—A rapid technical assay for lead has recently been described by E. J. Ericson.¹ The residues from the solution of most of the zinc, obtained as in the standard method, are dissolved in 10 c.c. of nitric acid, boiling to the disappearance of brown fumes. Then add 100 c.c. of water, 30 c.c. of ammonia, and 5 to 10 grams of ammonium persulphate, according to the amount of residue. Boil five minutes, settle ten minutes, and filter quickly through double 2 cm. filters, size 1 F. Wash four times with hot 10 per cent ammonia and five times with hot water. Place lead back in

¹ *J. Ind. and Eng. Chem.* **5**, 401 (1913); *Eighth Inter. Congress Appl. Chem.* **1**, 184.

beaker, add 25 c.c. of hydrogen peroxide (10 to 50 c.c. U. S. P. acid per liter plus 50 c.c. concentrated nitric acid). Stir until dissolved, add 15 c.c. of nitric acid (d., 1.2) and 75 to 100 c.c. of water, and titrate the excess of hydrogen peroxide by standard potassium permanganate (.568 gram per liter). If 25 c.c. of reagent does not dissolve all the lead, double the quantity and double the blank analysis. For zinc high in lead, the solution is checked against a standard spelter, tested by a standard method.

38. Separation of Cadmium in Trichloroacetic Acid. — This element is first separated from most of the zinc by hydrogen sulphide as in the standard method (35), and the first impure sulphide of cadmium is redissolved in hydrochloric acid. The solution, after filtering off traces of copper or lead sulphides and boiling out the hydrogen sulphide, is nearly neutralized with ammonia. Trichloroacetic acid, which dissociates less than mineral acids, is employed for the separation of the last traces of the zinc from the cadmium. A solution of 8 grams of the acid is added and the solution diluted to 200 c.c., and charged with hydrogen sulphide. The remaining operations are the same as in the standard method (35). The cadmium may also be titrated like zinc, in routine work. Dissolve the filtered sulphide, remove sulphur by a second filtration, oxidize with nitric acid, dilute and titrate with potassium ferrocyanide in the same way as for zinc, adding ferric chloride, citric acid, and ammonia. The ferrocyanide may conveniently be of the following value, — 1 c.c. equals .0025 gram of Cd.

PART V

PHYSICAL TESTS—GENERAL INFORMATION

CHAPTER XV

METALLOGRAPHY OF COPPER AND BRASS

Purpose of Examination. — In a general sense, metallography signifies the investigation and description of the structure of metals and their alloys, or is a science which determines the physical properties, microscopic appearance, and microstructure of an alloy, then ascertains how these factors are related to the thermal and mechanical treatment of the metal and to its chemical composition, finally considering the influence of defective treatments or of chemical impurities upon the metal during manufacture and use.¹ The microscope aids the vision to detect the finer structure and the camera fixes a record of the observation. Etching of the polished surface brings the more refractory constituents into relief and develops the structure.

As such tests are already a valuable assistance in foundries, some condensed description of practical metallography will recommend itself to those who are introducing microscopical examination in their work.² The art of photography must always be previously acquired. Many good treatises are accessible.³ The description is therefore confined principally to methods for the selection and preparation of samples of copper and its alloys for the microscope, adding some recommendations on special apparatus and its manipulation. The photomicrographs of alloys and formulas for etching were communicated by W. H. Bassett.

Crystallography. — When metals or alloys are cooled through the critical temperatures or points at which structural changes

¹ Le Chatelier & F. Osmond, *Metallographist*, 1, 5, 18, 65.

² See list of standard works in closing paragraphs.

³ *Modern Picture Making*, Eastman Kodak Co.

can occur, the crystals may be simple but are usually star-like or dendritic forms, masses, or crystallites with a vein filling of the more fusible eutectic mixtures. These forms are broken up by rolling or hammering and highly modified by quenching, annealing, or special reheating above critical temperatures. In the cooling of non-ferrous alloys from a liquid state, there is a progressive separation of one or more solid-solutions, the number formed depending on the chemical composition of the alloy and its heat treatment. There are also some differences in the judgment of observers as to the nature of the changes at transformation points in the cooling curves. The crystalline forms are designated by the signs for the letters *alpha*, *beta*, *gamma*, *delta*, etc.¹ (See micrographs.)

The constituents of alloys² may be present as: (1) free metals nearly pure; (2) solid solutions of one metal in another or of definite chemical compounds in excess of metal; (3) eutectic mixtures; (4) definite chemical compounds of metals with metals or non-metals; (5) allotropic modifications of 1 and 4. According to Charpy, the points of transition in copper-zinc alloys correspond to a series of definite compounds. Tafel³ considers that one compound, Cu_2Zn_3 , is proved and possibly CuZn . Sheperd⁴ holds that no definite compounds are formed in brasses, but that one to six solid solutions are possible according to conditions. Also that in bronzes, five solid solutions are possible, and that some alloys with much tin or aluminum may contain the compounds Cu_3Sn , or CuAl_2 . With solid alloys of silver and copper, crystallites of silver may hold 1 to 7 per cent of copper and a sensible amount of arsenic and antimony in solid solution,⁵ while copper crystallites may contain 1 to 2 per cent of silver, hence such crystallites cannot be assumed to be pure elements.

The structure of refined cast copper, when cooled directly from the molten condition, consists of primary crystallites of copper, partly surrounded or divided by thin seams filled with a mother liquor or eutectic mixture of copper and its suboxide ($\text{Cu} + \text{Cu}_2\text{O}$), containing 3.45 to 3.5 per cent of oxygen. The amount of eutectic increases with the oxygen and addition of

¹ *Metallographist*, **5**, 145; H. M. Howe, *Elect. Chem. and Met. Indust.* **7**, 423. H. O. Hofman, *Metallurgy of Copper*, Chapter IV.

² J. E. Stead, *Metallographist*, **5** (1902), 111.

³ *Metallurgie*, **5** (1908), 349.

⁴ *J. Phys. Chem.*, **8**, 421. *Metallurgie*, **1** (1904), 462; **5**, 349; **10**, 632.

⁵ *Metallographist*, **1**, 5, 18, 65. *Zt. Anog. Chem.* **49** (1908), 289.

oxidizable metallic impurities, until in highly oxidized or rabbled metal, the structure becomes coarse or indistinct and globules of the suboxide appear over the surface of the etched section.

1. The Selection of Samples. — It is advisable to orient, or measure and record, the exact position of each face of each test-piece taken from copper or alloys, with reference to the length and diameter of the casting, wire, or plate. Two photomicrographs are usually taken from each of two dissimilar faces of the small sawed cube or plate, selecting one parallel to the surface set or the longest dimension and one perpendicular to it. In foundry work, separate views may be taken for tests of defective metal with a magnification at the eye-piece of about 25 and 60 diameters which corresponds to a magnification of about 33 and 77 diameters respectively, as measured on the glass plate, or finished print. From 25 to 100 diameters are the usual limits for examination for physical defects, the higher powers up to immersion objectives being reserved for critical studies of individual crystals. The location of test-pieces is easily accomplished by observing a fixed system in stamping the test sample. This records the position of the etched faces with reference to the specimen and the length and width of the finished photomicrograph.

To secure any proper knowledge of the structure of cast metal, samples should be taken near the center of the casting, on the side near the "chill" and at top and bottom. A fair average position is considered to be just to one side of the longest median line with the upper face of the cube one-half inch below the upper surface and far enough from the ends to avoid the chilling effect of the mold. Pieces are usually taken from a plate or casting with a band-saw having ten teeth to the inch, and cooled by a stream of water or a blast of compressed air, which is directed upon the sample. As the crystalline aggregates appearing upon the surface of cast metal are very large and variable for reasons specified, the only way to learn much of value is to accumulate a large number of micrographs for comparative study, having all the physical and chemical data recorded upon the cards.

2. Polishing. — Good levigated powders are easily purchased. They may, however, be prepared from calcined ammonium alum, commercial flour emery, oxide of chromium from combustion of ammonium bichromate, and oxide of iron from the calcination

in air of ferrous oxalate.¹ To properly classify the fine powders by levigation, one-tenth per cent of nitric acid may be added to the water to dissolve calcium carbonate, etc. Stir, pour off, add distilled water, repeat several times, finally adding a little ammonia to help settling. After fifteen minutes, the coarse grains may be rejected, in one hour a coarse powder settles, in four

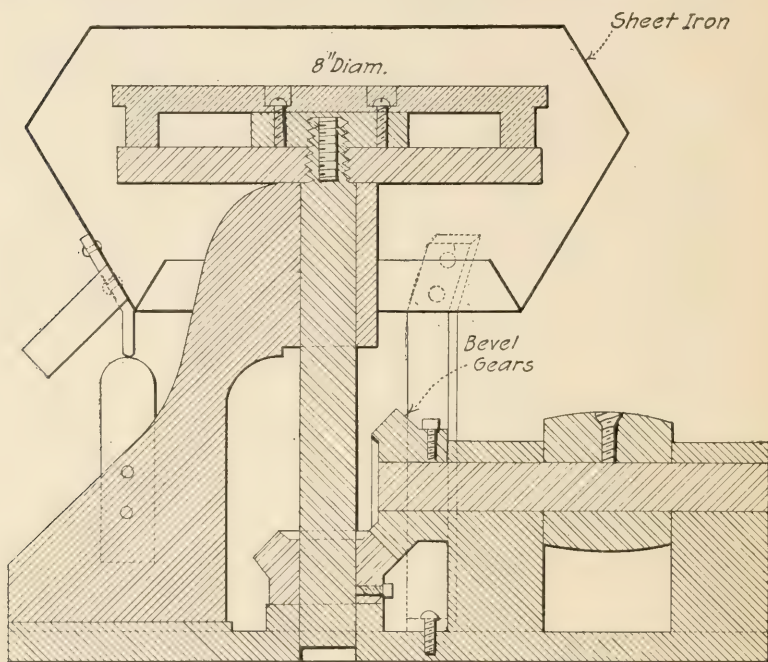


Fig. 17.—Polishing Disc.

hours a powder for iron, while as much as eight days may be required to settle the finest powders.

Treatment of Sample.—The sample is cut so that a surface $\frac{1}{4}$ inch (6 cm.) to $\frac{1}{2}$ inch (12.5 cm.) square can be filed. First it is filed smooth with a second cut file and then cross-filed with a very fine flat file to remove the first file marks. The polishing is then done on a wheel which makes at least 1800 revolutions per minute and has cloth-covered faces against which the sample is held. The polishing apparatus of Prof. C. R. Hayward illustrates one of the recent designs which protects the

¹ Chatelier & Schloesing, *Metallographist*, 5, 291.

operator from the mud produced by the fine stream of water with which the wheel is fed (Fig. 17). Zimmerschied and Aston have published similar designs.¹ A disc specially recommended consists of a brass plate with a half-inch rim and filled with solid paraffine wax.²

The first polishing is usually done on a wheel faced with canvas (such as 8-ounce duck), using a paste of flour emery and water, applied with a brush. Water is allowed to drip on the wheel during the polishing. The sample is again washed and applied to a wheel covered with heavy broadcloth (such as cloth for billiard tables), upon which fine tripoli and water is used. The sample is again washed and applied to a broadcloth, or wax-covered, wheel on which a thin paste of jeweller's rouge is used. Great care is taken in this final polishing to use the right amount of rouge, and the wheel is moistened slightly from time to time with water from a wash-bottle, so that finally the sample comes from the wheel polished free from scratches and quite dry, with no streaks of rouge on the polished surface. These conditions give the best results, for scratches are easily seen and no further washing (with the possibility of scratching the sample) is necessary. If the sample is one of cast copper containing oxygen, this method of finishing will bring out the oxide structure and but very little etching is then necessary to prepare it for the microscope.

3. Etching.—The etching of all samples of copper and brass is done in a mixture of hydrogen peroxide (perhydrol) and ammonia. Different mixtures are used for different copper content. (J. O. Handy has proposed to etch cast copper by a solution of ferric chloride in alcohol.)

Cast copper (containing oxygen) is taken as polished clean, without washing, held in platinum-tipped forceps and immersed with a stirring motion in a solution containing 5 parts by volume of ammonia (d., .90), 5 parts water, and 2 parts of Marchand's hydrogen peroxide. (If the 3 per cent peroxide of medical strength must be employed, omit the water.) Stirring is continued until the solution ceases to effervesce. The sample is then washed with water, wiped with clean soft cotton, dipped in alcohol if preferred, and dried. *Wrought copper*, either hard

¹ *J. Am. Chem. Soc.* **29**, 855, and *Elect. Chem. and Met. Indust.* **8**, 15.

² *Eng.* **90**, 108.

or annealed, is etched in the above manner, but using equal parts of water, ammonia, and (M) hydrogen peroxide. These proportions are not absolute, but are varied as experience and conditions indicate.

Brasses containing 85 per cent to 95 per cent copper are etched in exactly the same way as wrought copper. Brasses containing 63 per cent to 80 per cent copper are etched in a mixture of 5 parts ammonia, 5 parts water, and 2 parts of (M) hydrogen peroxide until the solution begins to effervesce (about 3 to 5 seconds' immersion). There is no definite point between 80 per cent and 85 per cent copper at which either of the above mixtures must be used instead of the other one described. *High brass*, containing less than 62 per cent copper, is first etched by electrolysis in a solution of ferrous sulphate, sodium sulphate, and sulphuric acid made up as follows: Dissolve 30 grams of ferrous sulphate (FeSO_4) and 4 grams of sodium hydroxide (NaOH) in 100 c.c. of water, then add 2000 c.c. of water and 100 c.c. of strong commercial sulphuric acid. The sample is held in platinum-tipped forceps hung on an electrolytic stand so that the sample just fails to touch the solution. By shaking the solution, it is made to touch the sample and the surface tension keeps this contact. The sample should not be dipped in the solution, but should be held so that the surface of the solution rises slightly to meet it. If the sample is immersed, the etching is not uniform. A current of about .1 ampere at 8 to 10 volts is necessary.

"Alpha and Beta" Constituents. — The "Beta" constituent in these brasses is colored reddish-brown by the electrolytic etching in about thirty seconds, but the "Alpha" constituent is not affected. These brasses become covered with a dark coating which can be wiped off with wet cotton. The sample is then washed with water and immersed in peroxide mixture (5: 5: 2) for a very short time, washed in water, dipped in alcohol, and dried. Brasses, consisting of pure "Beta" crystals only, etch best in the peroxide mixture just given. Only when "Alpha" and "Beta" crystals occur together, is it necessary to etch both by electrolysis and hydrogen peroxide mixture. German silvers are etched by electrolysis alone and seem to etch best in an old solution, i.e., one that is becoming saturated with dissolved metals from previous etching of brasses.

Coppers, brasses, or bronzes may be heat-tinted in the final polishing with rouge by allowing the wheel to run finally dry and become hot under the specimen. Practice is necessary to gauge the amount of dryness and pressure. Polishing in relief is also accomplished by long polishing with tripoli and rouge with a soft backing, or by heating copper in a current of pure hydrogen for 3 to 4 minutes (6).

For the new product, copper-clad steel, J. O. Handy recommends a boiling 25 per cent solution of potassium cyanide.

4. Apparatus for Photomicrographs.

— There are a number of good types in use in the United States and Europe. The one used by the author is designed by Sauvour and Boylston with a Bausch and Lomb microscope. For copper and brass, the usual combination of lenses desired in American microscopes consists of eye-pieces of (25, 50, 75 mm.) focal length, combined with a series of (16, 8, 4, 2 mm.) objectives, or a series of objectives according to the ($\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, and $\frac{1}{16}$ inch) system of focal lengths.

The sample is illuminated usually by a small prism or glass disc mounted within the lower part of the microscope just above the objective. Light from a small arc lamp with automatic feed passes through the side of the microscope and is reflected down upon the upper surface of the specimen by turning the milled head so that the disc sets at an angle of about 45 degrees. A movable mechanical stage is almost a necessity. A small magnetized holder is convenient for iron and steel. See Fig. 18.

The small arc lamp usually furnished is supplied with direct current from an ordinary wall socket through a special resistance coil. The light passes through condensing lenses and a cooling

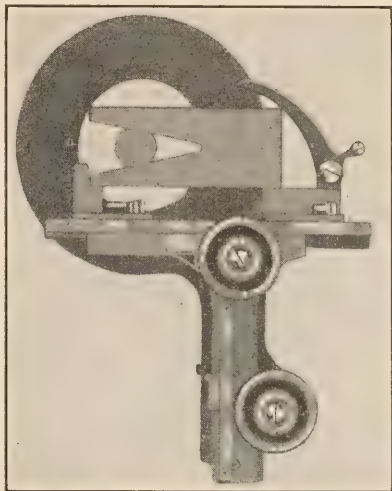


Fig. 18. — Movable Stage with Magnetized Holder.

cell, containing water and sufficient potassium chromate, or dichromate, to produce a pale yellow light with perhaps a greenish tint. An iris diaphragm shutter is placed in front of the lamp and a short distance from the microscope. For visual examination a piece of cobalt blue glass may be inserted back of the shutter.

5. Photography. — "Hammer Slow" plates, "Cramer's Isochromatic," or any other American or European plate of slow speed and with the quality of non-halation, may be employed and the exposure will vary from two to sixty seconds or more, according to the sample and the amount of potassium chromate or dichromate in the water-cooling cell of the electric lantern. The plates may be developed with any hydroquinone (or metol-hydro) developer, either separately or in a developing tank and fixed with a solution of sodium thiosulphate containing a little hardener. The tank method is said by one operator to give the finest negatives when the right conditions have been learned. The final prints are usually made on a rapid paper, such as Velox, by exposure in the dark room to the light of a tungsten lamp and finished according to manufacturers' formulas. The papers may then be rolled upon squeegee plates of japanned metal, if the smooth finish is preferred. The dry prints may be easily cut to uniform size by placing them on a soft wood block and stamping them with a steel die which is struck with a copper hammer. The small circles or squares are then mounted on stiff glazed cards. On the face of the cards, a printed form may be arranged in small neat type, to be filled in with the number of the specimen, the conditions of exposure, degree of magnification, position of the sample, and any analytical data required for a proper understanding of the subject photographed.

In order to show the general structure, or crystalline aggregates, in cast copper and also the internal structure of copper and eutectic, it is desirable to photograph the etched faces of cast copper with a low and a high power. The first combination used by the authors gives a magnification of 25 diameters at the eye-piece or about 33 diameters on the 4×5 inch glass plate in the holder. To determine the actual magnification, a photograph may be taken of a micrometer scale, or an image of the scale may be formed on the ground glass, and the distance of the lines measured on the plate.

Polished samples are mounted for the visual examination on a cover glass slide with a piece of wax, or in a special holder. The face should be very carefully leveled until it is exactly at right angles to the axis of the microscope. As already indicated, this instrument should be furnished with a movable stage which permits an immediate examination of the whole surface in order to select, in the case of copper particularly, an average structure for exposure. The focussing of the image upon the ground glass of the plate-holder must be necessarily very sharp or exact, and can only be determined by experiment. The sensitized plates are exposed to the yellow light of the illuminator from two to sixty seconds according to the subject, a matter determined also by experience. The plates should then be developed as soon as possible by regular photographic methods, producing as sharp contrasts and clear detail as possible.

A set of photomicrographs, furnished by W. H. Bassett, will illustrate the average types of commercial alloys and the appearance of good finished prints. Some structures of copper¹ are also included to show the marked differences between native mass copper and cast or rolled refined metal.

INDEX TO PHOTO-MICROGRAPHS (MAGNIFIED 77 DIAMETERS)

No.	Name	Condition and Heat Treatment	Copper Silver	Zinc
	<i>Copper</i>		Per cent	Per cent
1	Deoxidized	Native mass. Also by cast copper melted under charcoal.	99.97+
1b.	Deoxidized	Remelted and hard-rolled, refined.....	99.976
2	Half circle (with 3)	Hard-rolled refined, .072" thick.	99.927
3	(with 2)	Heated $\frac{1}{2}$ hour 600° C., quenched.....	99.927
4	Cast copper	High pitch refined ingot	99.945
5	<i>Brass</i>	Hard-rolled from 800° C.....	89.96	10.04
6	"	Heated $\frac{1}{2}$ hour 600° C., quenched.....	"	"
7	"	Heated as above, quenched....	80.18	19.82
8	"	" " " "	66.08	33.92
9	"	" " " "	60.63	39.37
10	Hard brass	Finished hard.....	56.25	43.75
11	(same as 10)	Heated $\frac{1}{2}$ hour 650° C., quenched	"	"
12	(like 10)	Heated as above, but slowly cooled	"	"

¹ Prepared by A. W. Senter.

6. Determination of Oxygen in Copper by Photomicrographs.

— Following several earlier attempts to estimate oxygen by planimetric measurement of the relative areas of copper and eutectic in a microscopic field, E. S. Bardwell has avoided such a tedious measurement by projecting the area of the field on a piece of paper and tracing the copper areas. The areas are then cut out with a shears and weighed. (See 15, Chapter XIII.)

7. Special Tests with Etched Samples. — (a) *Determination of Hardness of Micrographic Structures.*¹ — For the scratching of etched sections, one metallographist employs a set of needles standardized to Moh's mineral scale. The principal numbers are: lead, 1; tin with iron, 2; zinc, 2.5; copper, 3; bronze with 12 per cent tin, 3.5; iron wire, 3.7 to 3.9; sewing needles, 5 to 5.5; tempered yellow, 4; blue, 5; drill steel yellow, 6; chrome steel, 6 to 6.5; ferrochrome, 7 to 7.5° of hardness. Constituents may also be identified by color and behavior to reagents. The schleroscope or Brinell machine are now advocated and employed for working tests of metals.

(b) *Preservation of Etched Specimens.* — The etched faces may be carefully painted with a thin solution of jeweller's lacquer. A special varnish which is recommended, known as Zapon, is a solution of guncotton in amyl acetate. It permits the use of lenses of the highest power without removal of the coating (Le Chatelier).

(c) *Casting of Small Specimens.* — Small specimens of experimental alloys may often be melted in magnesia crucibles and cooled under charcoal, or cast on plate glass or steel. When glass gives too much trouble, such alloys may be cast on sheet mica.² Cut a funnel of good charcoal of the size of button desired, place it on a fresh sheet of mica, and pour in the alloy. Place the mold and metal on a fresh sheet, cover with some potassium cyanide, heat with a flame until upper surface of the metal softens, and quickly press down a third sheet upon the top of the alloy in order to obtain a good surface for polishing.

(d) *Determination of the Weakest Structure.* — The weakest part of a metal or alloy can be often ascertained by bending the etched microscopic section itself. This can be effected by placing the section, polished side down, over a V-space cut out of a

¹ Method of Behrens, *Metallographist*, **5**, 158.

² Method of H. J. Hannover, *Ibid.* **4**, 29. — *Le Chatelier* p. 17.

PLATE I

Fig. 1

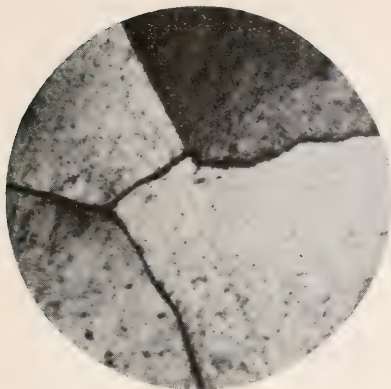


Fig. 2

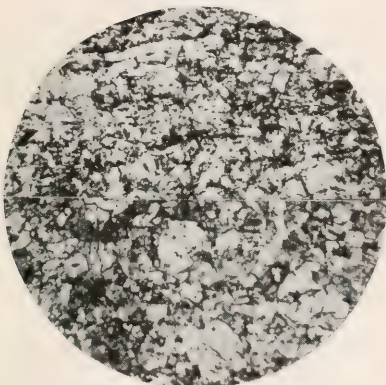


Fig. 3



Fig. 5

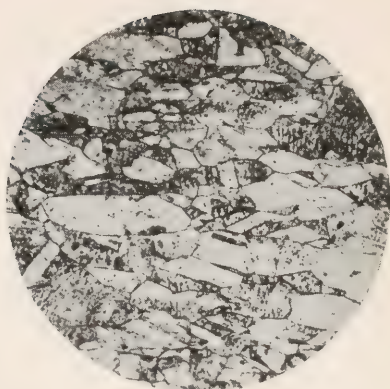


Fig. 1b

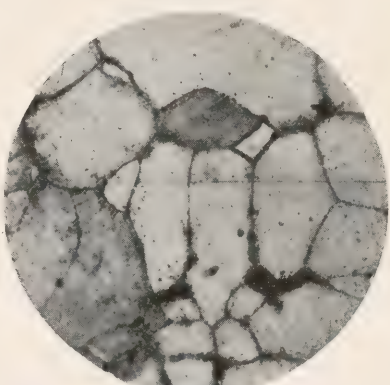


Fig. 4



Fig. 6

(Facing page 268)

PLATE II

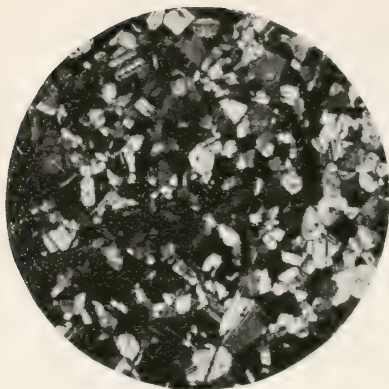


Fig. 7

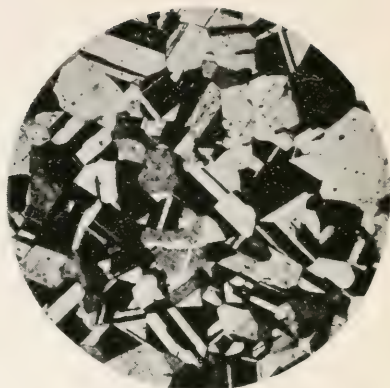


Fig. 8

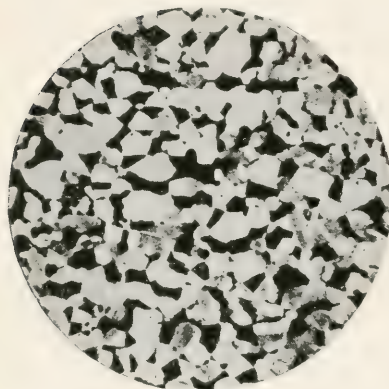


Fig. 9

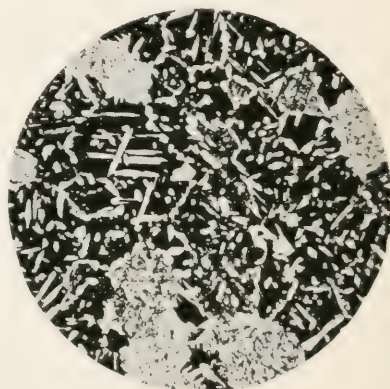


Fig. 10

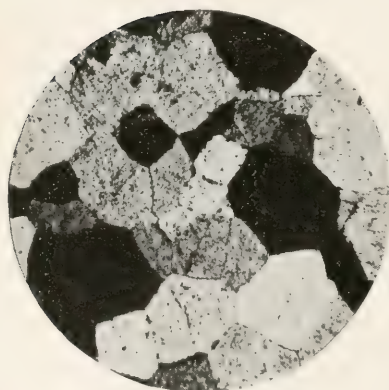


Fig. 11



Fig. 12

solid piece of steel and applying force to the back to bend the specimen. Even if the piece does not break off, the weak places often give way and it is easy to detect the zone of incipient fracture by examination under the microscope.¹

NOMENCLATURE — COMMON TERMS

Allotropic Modification signifies a change from the normal chemical and physical properties of a substance without any actual change in the composition.²

Alloy, Metallic. — An intimate mixture or union of metallic substances which on melting do not separate into distinct liquid layers (Stead).

Alpha State. — A term which has been applied by metallographists to the first type of solid solutions which may separate as crystals in the cooling of brass and other non-ferrous alloys. Not colored by acid electrolytic etching, a characteristic structure in (alpha) brass, 63 per cent copper and in bronze with less than 10 per cent of tin. See micrographs.

Atomic Volume. — The atomic weight of an element divided by its specific gravity.

Beta State. — The name is used with non-ferrous alloys to designate a second type of solid solution which may be formed as crystals in brass, etc., during cooling or by heat treatment; — colored by acid etching.³

Critical Point. — The point or zone of temperature at which some physical or chemical change takes place in the cooling or heat treatment of a metal or alloy. Sometimes indicated by evolution or absorption of heat.

Eutectic. — The solidified mother liquor, produced in the cooling and crystallization of metals, having a freezing point below that of either of the constituents.

Eutectic Point. — The point of intersection of two inclined branches and a horizontal line in the freezing point curve of metals with temperatures and percentage of constituents as co-ordinates. The horizontal line is called the eutectic line, and the alloy the eutectic.

¹ Due to J. E. Stead.

² Nomenclature of Microscopic Substances, etc., in Steel, *Int. Soc. for Testing Materials*, 1914.

³ *Inst. Metals*, 2 (1909), 1. *Metallurgie*, 1 (1904), 462.

Eutectoid. — The eutectoid is analagous to the eutectic in almost every way, differing from it simply in that the eutectoid point represents the intersection of two lines along which separation has taken place from a solid solution rather than from a liquid melt.¹

The eutectoid is the alloy of lowest transformation point.²

Gamma State. — The terms, alpha, beta, gamma, delta, etc., have all been applied to the solid solutions and mixtures successively formed in the cooling of brass and bronze from a liquid melt or by reheating and quenching in water. Consult standard references. Constituents α and β are ductile and malleable, but γ , δ (also ϵ and η if accepted) are increasingly brittle.

Isomorphous. — A term applied to crystals of similar form, or to a mixture crystallizing as a homogeneous whole.

Metarals. — Metallographists now define microscopic substances in two general classes: *First*, "metarals," — single phases, such as elements, chemical compounds, or solid solutions; *second*, "aggregates" or mixtures in the definite proportions of eutectics and eutectoids, or of indefinite proportions. In minerals, obsidian is a type of a solid solution, while mica, feldspar, and hornblende are aggregates.

Slip-bands. — A microscopic appearance in smooth surfaces of strained metals caused by slips along the cleavage or gliding planes of the crystalline grains.

Solid Solutions. — Solid "isomorphous mixtures" or "mixed crystals" of two or more substances, such as gold and silver, or copper with nickel, — metarals.

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² Howe and Levy, Report II, Vol. 2, 6th Int. Congress for Test. Materials.

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CHAPTER XVI

THE ELECTRICAL RESISTIVITY OF COPPER

MANUFACTURERS and consumers of copper know that very slight traces of some impurities have a most marked effect in lowering the percentage of electrical conductivity, or increasing the electrical resistivity of refined copper. For "Lake" copper (whose only notable impurity is arsenic), and for refined electrolytic brands, the test of the conductivity, or resistivity, of the annealed wire furnishes a rapid approximate determination of the arsenic (and antimony), which enables an operator to grade the metal and permit it to be delivered only for work in which that particular grade of metal can satisfy the requirements.

1. Apparatus for Measurement of Resistivity.—The types of low resistance "bridges" employed in mills and refineries are so varied in design and being so rapidly improved, that a description of anything but the latest form is inadvisable. In Germany, a Thomson bridge designed by Siemens & Halske is employed, the standard slide wire being made of German silver with a total resistance of .1 ohm. The percentage conductivity, hitherto, has been compared with the value for pure mercury given by the Reich Anstalt.

In America, more than twenty firms use a Hoope's, or Willyoung, instrument, in which a piece of copper wire about 1 meter in length is compared directly with copper standards whose resistance has been determined by the U. S. Bureau of Standards. A new form of a direct-reading conductivity bridge is the design of G. Grower of the American Brass Co., and made by Leeds & Northrup of Philadelphia. The wire is cut to a fixed length of 68.26 cm. before weighing and it is only necessary to subject the scale reading of conductivity to a correction for the percentage of variation of the sample from a standard weight of 20 grams.

The machine is less expensive than some other types, because it is only required to test the one size (.080 inch in diameter),

which has been adopted as a standard size for comparative tests by the principal American producers and consumers, and is prescribed in the copper specifications of the American Society for Testing Materials.¹

2. Density. — The “density” of copper is defined by the U. S. Bureau of Standards to be “the number of grams per cubic centimeter,” and is identically equal to the “specific gravity” of the copper at 20° (or other specified temperature), referred to water at its maximum density. This point is found at 4° C., at which degree a cubic centimeter of water weighs one gram. Example: A specific gravity of 8.914 at 20° C. is equal to a density of 8.8986. The value assumed by recent authorities is 8.89 for either hard- or soft-drawn wire. The average density of cast copper is about 8.55, but with native mass, or deoxidized copper melted in crucibles, the value is 8.925 to 8.935. Annealing shortens a rod or wire without changing the apparent density.

3. Resistivity. — This term, as generally adopted, signifies the electrical resistance in international ohms of 1 meter of wire weighing 1 gram, or resistance per “meter-gram,” measured at the standard temperature of 20° C. This is obtained by multiplying the weight of one meter of the wire by the electrical resistance of one meter at 20° C., calculated from the observed resistance of the length of sample actually tested. The value for the resistivity of copper wire assumed to have 100 per cent conductivity, was first accurately determined by Matthiesen in 1860, but copper wire is now produced testing 102 per cent conductivity, and native mass or cathodes may test up to 103 per cent by his standard. See table of data on the next page.

As resistance measurements cannot be made at a fixed temperature in practice, it is necessary with a German silver standard to reduce the observations to the standard temperature of 20° C., or whatever value is assumed as standard. When the bridge standard is an annealed copper wire of nearly 100 per cent “conductivity,” no temperature correction is necessary in tests of high-grade metal of 97 per cent “conductivity,” or better. When arsenical, or low-grade casting metal is tested at variable temperatures against a fixed copper wire standard

¹ *Year Book*, 1914.

of 100 per cent conductivity, it is necessary to apply a correction to reduce the reading to the standard temperature of the bridge. A table of corrections may be determined for each instrument by cooling the testing room in winter down to the freezing point and testing a set of copper wire samples which will cover the material ordinarily tested. These tests are repeated on the same samples as the temperature rises through a range of 50° F.

4. Temperature Coefficient.—The U. S. Bureau of Standards has determined that the temperature coefficient of electrical resistance is proportional to the electrical conductivity of copper, for values over 97 per cent.¹ The author has determined by the above method that the value for temperature coefficient is also true for wire produced from furnace-refined copper, down to a limit of 30 per cent conductivity, or even less, when the principal impurity is arsenic.² In other words, the coefficient, which the Bureau assumes to be .00394 per degree Centigrade, is strictly proportional to the “conductivity” by Matthiessen’s standard whatever the purity of the copper. This is probably true for electrolytic copper, which contains traces of other impurities, such as antimony.

CALCULATION OF RESISTIVITY

5. Rule 1.—A resistance R at temperature t is corrected to the standard temperature of 20° C. by applying the temperature coefficient at 20° C. (termed C_{20}) in the formula:

$$R_t = R_{20}(1 + C_{20}[t - 20]).$$

This coefficient applies only to 20° as a standard. For the calculation of coefficients to other specified temperatures, see reference (1). The (20°) temperature coefficient for copper of 100 per cent conductivity is .00394 per degree Centigrade, according to the U. S. Bureau of Standards.

Rule 2.—The Bureau also shows the relation between the percentage of electrical conductivity and temperature coefficient and the reduction of resistivity to standard temperature by the following statement: The change of resistivity (not resistance)

¹ J. H. Dellinger, Reprint 147, *Bull. U. S. Bureau of Standards*, Vol. 7, No. 1.

² Circular 31, *U. S. Bureau, Copper Wire Tables* (1912).

per degree Centigrade of a sample of copper is .000598 (international) ohm per meter-gram, or .00681 micro-ohm per Centimeter cube.

Rule 3. — The resistivity in international ohms corresponding to 100 per cent conductivity, Matthiesen standard, was fixed at .153022 by the American Institute of Electrical Engineers and the U. S. Bureau of Standards. Within the last two years, Government Bureaus have agreed upon a new value, .15328, which is about .17 per cent lower, if calculated in terms of conductivity. The tendency with large concerns, at present, is to report specifications to outside parties in terms of "resistivity," rather than the debatable value of "conductivity."

The percentage "conductivity" of a sample of copper by length and weight, or meter-gram system, is obtained by dividing .153022 (or the latest international value of .15328) by the "resistivity" of the sample tested.

6. Notes on the Determination of Resistivity of Wire. —

Until comparative investigations by the Government Bureau and leading copper concerns were recently undertaken, the lack of agreement in measuring instruments and the tendency to rush work without any adequate precautions to secure an exact agreement of temperature between the test samples and the standard bridge wire were the cause of serious discrepancies between producers of copper and manufacturers, or consumers, of wire. Another variation resulted from the practice in rolling mills of testing hard-drawn wire and calculating the resistance by the measurement of the average cross-section. As long stretches of wire are seldom perfectly round, such a value is more or less inaccurate, and the standard specifications of the American Society for Testing Materials now provide that all tests, in case of disagreement between two parties, shall be made on wire of .080 inch diameter by the meter-gram system.

Each instrument should be provided with a set of extra wires, whose resistance has been certified by a national Bureau of Standards. One of these wires may then be placed upon the bridge each day to detect any change in the instrument. Wire samples are cleaned and straightened, and placed within the case of the bridge. Fifteen minutes ought to be allowed for the samples to attain the temperature of the closed case, after which they may be tested at the rate of about one in five min-

utes without raising the temperature. If the wire is touched with the bare hands in making the connections, the resistance may be raised as much as .4 per cent. All wires should be brightened, if necessary, at the points where connections are made with knife-edge contacts, by rubbing with a little chamois skin and precipitated chalk. The machine standards, etc., are cleaned with the soft skin, only.

R. F. Wood¹ has devised a very simple straightener for short lengths of copper wire. It consists of a (36" \times 5" \times 1.5") cast-iron slab faced on the lower side with a smooth hard-wood board, one inch thick. The slab is fitted with two straight iron handles on the edge facing the operator, and the wires are rolled under this weight a few times upon a second smooth board which rests on a small work-table.

The electrical conductivity of hard-drawn copper wire is ordinarily about 2.5 to 2.7 per cent lower than that obtained on the same samples when annealed. It is a well-known fact that this difference is relative and variable and depends first on the conditions of manufacture, and secondly on the grade of the copper, whether it is high-grade, or extremely arsenical. As the conductivity of copper wire is reduced by the presence of arsenic, etc., we finally reach a point (which according to the author's experiments lies between 64.5 and 62.5 per cent conductivity) where the conductivity of the hard-drawn and annealed wire from the same sample have the same value. Below this conductivity, the hard-drawn wire will have a value above the annealed, although the difference increases slowly. Conductivity tests of 64.5 per cent and 62.5 per cent correspond to .16 per cent and .18 per cent of arsenic, respectively.

By making a large number of determinations of the "conductivity" of samples of wire (both annealed and hard-drawn) in which the arsenic has been determined (or the arsenic and antimony in the case of electrolytic copper), a curve of reasonable accuracy may be plotted with the conductivities as ordinates and the percentages of arsenic as abscissæ. From this curve, the percentage of arsenic may be quickly taken with sufficient accuracy for many purposes. The time of wire-drawing and testing need not exceed one-half hour for single samples. Such a chart, covering a range from 103 per cent down to 30 per cent con-

¹ Formerly chemist, Quincy Smelting Works.

ductivity, has been prepared and used by several companies for the rapid grading of refined copper. Lawrence Addicks has plotted charts showing the effect of different impurities on copper, but the determinations were made on crucible-melted copper, which is practically deoxidized in the process. The values obtained with metal remelted in crucibles may be 1 to 4 per cent lower than the conductivity of furnace-refined copper containing the same amount of the special impurity in question. Refined metal from which most of the arsenic has been removed by long rabbling with soda-lime flux, will show a trifle higher conductivity, than untreated copper having the same percentage of arsenic.

STANDARD SPECIFICATIONS FOR COPPER

The following paragraphs summarize the chemical and electrical requirements included in the specifications for ordinary forms of "Lake" and "electrolytic" cast and wrought copper, which were adopted August 25, 1913, by the American Society for Testing Materials, and have been reprinted in the Year Book for 1914.

7. Electrical Requirements.—In order to be classed as "Lake," the copper must originate on the northern peninsula of Michigan, U. S. A. Lake copper offered for electrical purposes, whether fire or electrolytically refined, is termed "Low Resistance Lake." Such Lake wire bars, or "Electrolytic" wire bars, are permitted to have a resistivity not to exceed .15535 international ohm per meter-gram at 20° C. (as shown by test on annealed wire). All ingots and ingot bars are permitted to have a resistivity not to exceed .15694 ohms per meter-gram at 20° C. (annealed). Cakes, slabs, and billets come under the ingot classification, except when specified for electrical use when purchased, which would bring them under a wire-bar classification. Lake copper having a resistance greater than .15694 int. ohm per meter-gram at 20° C., is termed "High Resistance Lake." Its quality is due to arsenic, without other foreign elements.

8. Chemical Requirements.—"Electrolytic" copper and "Low Resistance Lake" copper are required to have a purity of at least 99.88 per cent as determined by electrolytic assay, silver being counted as copper. "High Resistance Lake" copper is required to have a purity of at least 99.88 per cent, — copper,

silver, and arsenic being counted together; the limiting amount of arsenic being a subject of agreement at the time of purchase.

The remaining paragraphs of the complete specifications deal with the physical requirements, allowable errors in weights, and variations in sizes of cast copper plates or wire, and finally the manner of presentation, investigation, and settlement of claims.

INTERNATIONAL ATOMIC WEIGHTS FOR 1916

Element- Name	Sym- bol	Atomic Weight	Loga- rithm	Name of Element	Sym- bol	Atomic Weight	Loga- rithm
Aluminum	Al	27.1	1.43297	Molybdenum	Mo	96.0	1.98227
Antimony	Sb	120.2	2.07990	Neodymium	Nd	144.3	2.15927
Argon	A	39.88	1.60075	Neon	Ne	20.2	1.30535
Arsenic	As	74.96	1.87483	Nickel	Ni	58.68	1.76849
Barium	Ba	137.37	2.13789	Niton, emana.	Nt	222.4	2.34714
Bismuth	Bi	208.0	2.31806	Nitrogen	N	14.01	1.14644
Boron	B	11.0	1.04139	Osmium	Os	190.9	2.28081
Bromine	Br	79.92	1.90266	Oxygen	O	16.0	1.20412
Cadmium	Cd	112.4	2.05077	Palladium	Pd	106.7	2.02816
Cæsium	Cs	132.81	2.12323	Phosphorus	P	31.04	1.49192
Calcium	Ca	40.07	1.60282	Platinum	Pt	195.2	2.29048
Carbon	C	12.00	1.07918	Potassium	K	39.1	1.59218
Cerium	Ce	140.25	2.14691	Praseodymium	Pr	140.9	2.14891
Chlorine	Cl	35.46	1.54974	Radium	Ra	226.4	2.35488
Chromium	Cr	52.0	1.71600	Rhodium	Rh	102.9	2.01242
Cobalt	Co	58.97	1.77063	Rubidium	Rb	85.45	1.93171
Columbium	Cb	93.5	1.97081	Ruthenium	Ru	101.7	2.00732
Copper	Cu	63.57	1.80325	Samarium	Sa	150.4	2.17725
Dysprosium	Dy	162.5	2.21085	Scandium	Sc	44.1	1.64444
Erbium	Er	167.7	2.22453	Selenium	Se	79.2	1.89873
Europium	Eu	152.0	2.18184	Silicon	Si	28.3	1.45179
Fluorine	F	19.0	1.27875	Silver	Ag	107.88	2.03294
Gadolinium	Gd	157.3	2.19673	Sodium	Na	23.0	1.36173
Gallium	Ga	69.9	1.84448	Strontium	Sr	87.63	1.94265
Germanium	Ge	72.5	1.86034	Sulphur	S	32.06	1.50596
Glucinum	Gl	9.1	0.95904	Tantalum	Ta	181.5	2.25888
Gold	Au	197.2	2.29491	Tellurium	Te	127.5	2.10551
Helium	He	4.00	0.60206	Terbium	Tb	159.2	2.20194
Holmium	Ho	163.5	2.21352	Thallium	Tl	204.0	2.30963
Hydrogen	H	1.008	0.00346	Thorium	Th	232.4	2.36624
Indium	In	114.8	2.05994	Thulium	Tm	168.5	2.22660
Iridium	Ir	193.1	2.28578	Tin	Sn	118.7	2.07445
Iodine	I	126.92	2.10353	Titanium	Ti	48.1	1.68215
Iron	Fe	55.84	1.74695	Tungsten	W	184.0	2.26482
Krypton	Kr	82.92	1.91866	Uranium	U	238.2	2.37694
Lanthanum	La	139.0	2.14301	Vanadium	V	51.0	1.70757
Lead	Pb	207.2	2.31597	Xenon	Xe	130.2	2.11461
Lithium	Li	6.94	0.84136	Ytterbium	Yb	173.5	2.23930
Lutecium	Lu	175.0	2.24304	Yttrium	Yt	89.0	1.94939
Magnesium	Mg	24.32	1.38596	Zinc	Zn	65.37	1.81538
Manganese	Mn	54.93	1.73981	Zirconium	Zr	90.6	1.95713
Mercury	Hg	200.6	2.30233				

CHEMICAL CONVERSION TABLE

Elements	Compounds Weighed	Required	Factors	Logarithms
Aluminum	Al_2O_3	Al	.53033	-1.72455
	AlPO_4	Al	.22188	-1.34612
	AlPO_4	Al_2O_3	.41837	-1.62156
Arsenic	3 Ag	As	.23162	-1.36478
	As_2O_3	As	.75748	-1.87937
	As_2S_3	As	.60918	-1.78475
	$\text{Mg}_2\text{As}_2\text{O}_7$	As	.48274	-1.68372
	$\text{Mg}_2\text{As}_2\text{O}_7$	As_2O_3	.63730	-1.80434
	$\text{Mg}_2\text{As}_2\text{O}_7$	As_2S_3	.79244	-1.89897
Antimony	Sb_2O_4	Sb	.78975	-1.89749
	Sb_2S_3	Sb	.71424	-1.85384
	Sb	Sb_2O_5	1.33280	0.12477
Barium	BaCO_3	Ba	.69600	-1.84261
	BaCO_3	BaO	.77707	-1.89046
	BaCrO_4	Ba	.54217	-1.73414
	BaCrO_4	BaO	.60532	-1.78198
	BaSO_4	Ba	.58848	-1.76973
	BaSO_4	BaO	.65702	-1.81758
	BaSO_4	BaCO_3	.84552	-1.92712
Bismuth	Bi_2O_3	Bi	.89656	-1.95258
	BiOCl	Bi	.80166	-1.90399
	Bi_2S_3	Bi	.81221	-1.90972
Bromine	AgBr	Br	.42556	-1.62896
Cadmium	Cd	CdO	1.14235	0.05780
	CdS	Cd	.77807	-1.89103
	CdSO_4	Cd	.53919	-1.73174
	$\text{Cd}_2\text{P}_2\text{O}_7$	Cd	.56358	-1.75096
Calcium	CaSO_4	CaO	.41188	-1.61477
	CaO	CaCO_3	1.78473	0.25157
	CaSO_4	CaF_2	.57350	-1.75853
	CaO	CaF_2	1.39237	0.14375
(titration)	$\text{Na}_2\text{C}_2\text{O}_4$	CaO	.41843	-1.62162
Carbon	BaCO_3	C	.06080	-1.78390
	BaCO_3	CO_2	.22293	-1.34817
	CO_2	C	.27273	-1.43573
Chlorine	AgCl	Cl	.24738	-1.39336
	NaCl	Cl	.60657	-1.78288
Chromium	BaCrO_4	Cr	.20523	-1.31224
	BaCrO_4	Cr_2O_3	.29996	-1.47706
	BaCrO_4	CrO_3	.39468	-1.59625
	Cr_2O_3	Cr	.68421	-1.83519
	PbCrO_4	Cr	.16089	-1.20653
	PbCrO_4	Cr_2O_3	.23515	-1.37135
	PbCrO_4	CrO_3	.30941	-1.49053
Cobalt	CoO	Co	.78658	-1.89574
	Co	CoO	1.27132	0.10425
	CoSO_4	Co	.38038	-1.58022
Copper	Cu_2S	Cu	.79862	-1.90234
	Cu	CuO	1.25169	0.09750
	Cu	Cu_2O	1.12585	0.05148
	$\text{Cu}_2(\text{SCN})_2$	Cu	.52260	-1.71817
	$\text{CuSO}_4(5\text{H}_2\text{O})$	Cu	.25457	-1.40581

CHEMICAL CONVERSION TABLE — *Continued*

Elements	Compounds Weighed	Required	Factors	Logarithms
Fluorine.....	CaF_2	F.....	.48674	-1.68730
	CaSO_4	F_227914	-1.44582
	CaO	CaF_2	1.39236	0.14375
Hydrogen.....	H_2O	H.....	.11190	-1.04883
Iodine.....	AgI	I.....	.54055	-1.73284
	KI.....	I.....	.76449	-1.88337
Iron.....	Fe_2O_3	Fe.....	.69940	-1.84473
	Fe.....	FeO	1.28653	0.10942
	FeO	Fe_2O_3	1.11136	0.04586
	Fe_2O_3	Fe_3O_496660	-1.98525
Lead..... (electrolysis)	PbSO_4	Pb.....	.68324	-1.83457
	PbO_2 (210–230°C.)	Pb.....	.86430	-1.93667
	PbO_2 (theory)	Pb.....	.86622	-1.93763
	PbCrO_4	Pb.....	.64109	-1.80692
	PbO_2	PbS.....	1.00025	0.00011
	$\text{Mg}_2\text{P}_2\text{O}_7$	Mg.....	.21843	-1.33931
Magnesium.....	$\text{Mg}_2\text{P}_2\text{O}_7$	MgO36213	-1.55886
	MnO_2	Mn.....	.63189	-1.80064
Manganese.....	$\text{Mn}_2\text{P}_2\text{O}_7$	MnO_261231	-1.78697
	$\text{Mn}_2\text{P}_2\text{O}_7$	MnO49961	-1.69863
	$\text{Mn}_2\text{P}_2\text{O}_7$	Mn.....	.38691	-1.58761
	Ni.....	Nio.....	1.27267	0.10472
Nickel.....	Ni($\text{C}_8\text{H}_{14}\text{O}_4\text{N}_4$).....	Ni.....	.20316	-1.30784
	Am. Phos. Molyb.....	P.....	.01630	-2.21219
	$\text{Mg}_2\text{P}_2\text{O}_7$	P.....	.27874	-1.44520
Phosphorus.....	$\text{Mg}_2\text{P}_2\text{O}_7$	P_2O_563793	-1.80477
	K_2PtCl_6	Pt.....	.40151	-1.60370
Platinum.....	K_2PtCl_6	K_2O19376	-1.28726
Potassium.....	Pt.....	K_2O48258	-1.68357
	$\text{K}_2\text{Pt}_2\text{Cl}_6$	KCl.....	.30673	-1.48676
	SiO_2	Si.....	.46932	-1.67147
Silicon.....	SiO_2	SiO_3	1.26534	0.10221
Silver.....	AgBr	Ag.....	.57444	-1.75924
	AgCl	Ag.....	.75262	-1.87658
	AgI	Ag.....	.45945	-1.66223
Sodium.....	AgCl	NaCl40784	-1.61049
	AgCl	Na_2O43254	-1.63603
	NaCl	Na_2O53028	-1.73451
Sulphur.....	BaSO_4	S.....	.13735	-1.13778
	BaSO_4	SO_334297	-1.53526
Tellurium.....	Te.....	TeO_2	1.25098	0.09725
Tin.....	SnO_2	Sn.....	.78766	-1.89634
	Sn.....	SnO_2	1.26959	0.10366
Tungsten.....	WO_2	W.....	.85185	-1.93036
	WO_3	W.....	.79310	-1.89933
Zinc.....	ZnS	Zn.....	.67094	-1.82668
	ZnO	Zn.....	.80337	-1.90492
	$\text{Zn}_3\text{P}_2\text{O}_7$	Zn.....	.42891	-1.63237

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